Université de Toulouse

THÈSE

En vue de l'obtention du

DOCTORAT DE L'UNIVERSITÉ DE TOULOUSE

Délivré par :
Institut National Polytechnique de Toulouse (INP Toulouse)

Discipline ou spécialité :

Génie des Procédés et Environnement

Présentée et soutenue par :
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le : 10 Mai 2010

Titre :

Particle sizing and product quality in production of fine and nano particles by means of wet grinding process

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Ecole doctorale :
Mécanique, Energétique, Génie civil et Procédés (MEGeP)

Unité de recherche :
Laboratoire de Génie Chimique, Toulouse France.

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Dedicated to my parents

Acknowledgements

First and foremost, I would like to thank the supervisor of my thesis, Dr. Christine FRANCES deep from my heart for her valuable guidance, great help and dedicated support on this study.

I am quite grateful to Higher Education of Pakistan for the scholarship that permitted me to undertake this study.

I am grateful for kind help and administrative support of “Société française d'exportation des ressources éducatives (SFERE)” for my studies in France.

I would like to thank my colleagues Madam Mallorie TOURBIN, Madam Sylvie SHETRITE and Mr. Soualo OUATTARA for their kind support in different aspects of my work.

I cannot forget to thank technical and administrative teams of Laboratoire de Génie Chimique, for their untiring and steady support in the laboratory.

I would also like to thank to my father (late), mother, my brothers & sister for their endless love and constant support throughout my academic career.

Muhammad Asif Inam

Abstract

Wet grinding process is an interesting means of producing fine and nano particles. The particle sizing plays an important role in interpretation, control and optimization of various aspects of the wet grinding process. There is a lack of knowledge in understanding different aspects of particle sizing during a wet grinding process. The particle sizing in a wet grinding process is typical in the sense: (i) The dispersions in a wet grinding process, often, involve additives and (or) impurities. It is less known how impurities and additives influence the particle size of the dispersions in the wet grinding process. (ii) In a wet grinding process, dispersions of different concentrations may be used. It is less known how dispersions of different concentration may influence the particle sizing in a wet grinding process. (iii) In a wet grinding process, the change in average particle size of the product is rapid due to relatively fast breakage of the particles. (iv) The degree of poly dispersity in product changes with grinding time. (v) The nature of interaction between particles is non-colloidal before grinding process; this interaction becomes colloidal after a certain grinding time. Similarly, there is a lack of knowledge to understand how quality of final ground product is influenced in a wet grinding process. This study investigates the different aspects of particle sizing and product quality of aqueous dispersions of $CaCO_3$ in a wet grinding process carried out in a stirred media mill. Acoustic attenuation spectroscopy that is known for measuring particle size of dispersions on line, under real process conditions and without diluting the sample has been employed in the study in addition to the technique of dynamic light scattering. The study brings out the conditions in which the effects of impurities and additives etc. on particle size of the dispersions may be determined using acoustic attenuation spectroscopy. Furthermore, the study compares and analyze the particle sizing results obtained though acoustic attenuation spectroscopy and dynamic light scattering. The causes of differences in the results of two techniques have been investigated. We report presence of multiple scattering at high concentration of the dispersions during wet grinding process that result in misleading results of the particles sizes. Quality is an intangible concept. In order to understand how different operating parameters influence product quality, we propose a method based upon the definition of quality as defined in ISO 9000:2005. The method takes into consideration the important operating parameters of wet grinding process (such as the operating condition of the mill, the measurement of particle size and the material) and important product characteristics (such as average particle size, range of width of particle size distribution, stability of dispersion, degree of impurities, specific energy input and physical appearance). We bring out how a relationship between operating parameters and products of different grades may be established in a wet grinding process.

Key words: Acoustic attenuation spectroscopy, colloids, dynamic light scattering, fine and nano particles, impurities, product quality, stirred media mill and wet grinding process.

Résumé (abstract in French)

Le procédé de broyage en voie humide est une opération intéressante permettant la production de particules fines ou de nanoparticules. La caractérisation de la taille des particules est une donnée essentielle pour l'interprétation des données, le contrôle et l'optimisation de ces procédés selon divers aspects. Il y a un manque de connaissances relatif à la caractérisation de la taille de particules en relation avec les procédés de broyage en voie humide. Cette caractérisation est spécifique pour différentes raisons. (i) Les dispersions traitées par broyage contiennent souvent des impuretés et (ou) des additifs. Nous savons assez peu comment les impuretés et les additifs influencent la taille des particules en suspension dans ces procédés. (ii) Lors de procédés de broyage en voie humide, des dispersions de différentes concentrations peuvent être utilisées. Il est important de savoir comment la concentration de la dispersion peut influencer la mesure de la taille des particules lors du procédé. (iii) La modification de la taille moyenne des particules, résultant de leur fragmentation, est rapide. (iv) Le degré de polydispersité dans le produit change au cours du temps. (v) La nature des interactions entre les particules change; avant broyage les particules sont non-colloïdales, elles le deviennent après un certain temps d'opération. De même, il y a un manque de connaissances permettant de comprendre comment la qualité du produit broyé final est affectée lors du broyage. Dans cette étude nous explorons plusieurs aspects de la caractérisation de taille et de la qualité du produit au cours d'un procédé de broyage en voie humide du CaCO3, réalisé à l'aide d'un broyeur à billes agité. La spectroscopie acoustique qui est une technique connue pour ses potentialités en matière de caractérisation de taille de dispersions en ligne, sous des conditions réelles de procédés et sans nécessiter une dilution des échantillons, a été utilisée dans cette étude en complément de la diffusion dynamique de la lumière. Ce travail a montré sous quelles conditions les effets des impuretés et des additifs etc. sur la taille des particules en suspension pouvaient être déterminés par spectroscopie acoustique. De plus, nous avons comparé et analysé les résultats des mesures de taille obtenus avec les deux techniques. Les différences observées ont été analysées. Nous avons montré que la diffusion multiple observée à forte concentration en solide lors des procédés de broyage en voie humide pouvait conduire à une mauvaise interprétation des résultats relatifs à la taille des particules. En outre, la qualité est un concept relatif. Dans ce travail, nous avons adopté une démarche pour mesurer les effets de différents paramètres sur les caractéristiques du produit broyé en se basant sur une définition de la qualité telle que dans la norme ISO 9000 :2005. La démarche a permis de prendre en compte différents paramètres opératoires importants (tels que les conditions de fonctionnement du broyeur, la mesure de la taille des particules et les propriétés du matériau), ainsi que différentes propriétés caractéristiques du produit (comme la taille moyenne des particules, la largeur de la distribution de taille, la stabilité de la dispersion, le taux d'impuretés, l'énergie spécifique apportée au système et l'apparence visuelle du

produit). Nous avons montré que nous pouvions établir une relation entre les paramètres opératoires et différentes qualités de produits obtenus par un procédé de broyage en voie humide.

Mots clés : Broyeur à billes agité, colloïdes, diffusion dynamique de la lumière, impuretés, particules fines et nanoparticules, procédé de broyage en voie humide, qualité du produit et spectroscopie acoustique.

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a_1	Radius of particle 1 (m)
a_2	Radius of particle 2 (m)
A_0	Initial amplitude of a sound wave (m)
A_H	Hamaker constant (J)
A_x	Amplitude in a sound wave after a distance x (m)
C_s	Weight concentration (-)
C_v	Volume concentration (-)
d (H)	Hydrodynamic diameter (m)
d_{GM}	Diameter of the grinding media (m)
D	Translational diffusion coefficient (m^2/s)
D	Interparticle distance (m)
e	Electronic charge (C)
E_m	Specific energy (J/Kg)
F_A	Attractive force between the particles (N)
G_a	Attractive energy between two individual atoms or molecules (J)
G_{el}	Energy of repulsion (J)
h	Surface-surface separation between the particles (m)
k	Boltzmann constant (J/K)
l	Correlation length (m)
n	Refractive index of dispersant (-)
n_0	Number of ions of each sort in the bulk phase (-)
n_∞	Bulk density of ions (Kg. m^{-3})
N_c	Number of media contacts (-)
N_{GM}	Number of grinding media (-)
N_p	Number of feed particles inside the mill (-)
r	Interatomic distance (m)

SI	Stress intensity (J/kg)
SN	Stress number (-)
T	Absolute temperature (K)
V_A	Total intersection energy (J)
V_{GC}	Volume of grinding chamber (m^3)
Z	Valency of ions (-)
α	Attenuation coefficient (db/m)
γ	Reduced surface potential (V)
ε	Porosity of the bulk grinding media (-)
ε_0	Permittivity of free space (F/m)
ε_r	Relative permittivity (F/m)
η	Viscosity (Pa . s)
θ	Scattering angle (rad)
κ	Debye–Hückel parameter (m^{-1})
λ_o	Wavelength (m)
τ	Time difference (the sample time) of the correlator (s)
φ_{GM}	Filling ratio of grinding media (-)
Ψ_0	Surface potential (V)

Introduction

As per requirements of the university, the translation of chapter 1in French has been provided in the beginning of chapter 1.

I Introduction (en français)

I.1 Contexte et motivations

La demande de production de dispersions de particules fines ou ultrafines (nanoparticules) augmente jour après jour. Ces dispersions ont de très nombreuses applications dans beaucoup de domaines, tels que les peintures, les pigments, le papier, les adhésifs, les catalyseurs, les matériaux absorbants, les encres d'imprimerie, les émulsions, les crèmes, les céramiques, le ciment, les fibres, les charges pour les plastiques, les matériaux pour le traitement de l'eau, les agents blanchissants et les cosmétiques etc. Les particules fines et ultrafines ont, en raison de leur faible taille et du rapport surface/volume très élevé, des propriétés physico-chimiques exacerbées, qui diffèrent de celles des atomes ou des molécules les constituant mais qui sont aussi différentes de celles du matériau macroscopique. Ces propriétés induisent généralement une amélioration de l'homogénéité, de la solubilité, des propriétés rhéologiques, de la résistance mécanique ou de la réactivité par rapport aux produits de dimension plus élevée.

Il y a deux approches générales permettant la production de particules fines ou de nanoparticules: (i) les méthodes dites « bottom-up » (dans lesquelles les nanoparticules peuvent être produites par réaction, condensation ou agrégation de molécules etc.). (ii) les méthodes dites « top-down » (dans lesquelles on trouve les procédés par broyage qui à partir de particules grossières permettent d'obtenir des particules fines). Cette étude est associée à une méthode de type « top-down ». Dans cette approche, les procédés de broyage en voie sèche et ceux en voie humide sont deux options possibles. Cette étude a trait au procédé de broyage en voie humide pour la production de particules fines ou de nanoparticules. La technologie support de cette étude est celle des broyeurs à billes agités. Cette technologie est en effet une technologie prisée dans le domaine du broyage en voie humide car elle présente beaucoup d'avantages : une faible tendance à l'agglomération des fragments produits, des pertes de matière faibles, une oxydation moindre du produit, une plus grande facilité pour le traitement de matériaux toxiques ou encore le fait qu'il n'est pas nécessaire de mettre en place une technique pour l'élimination des poussières contenues dans l'air.

Dans les procédés de production de nanoparticules, la mesure de la taille des particules joue un rôle important. Récemment, plusieurs techniques ont été développées pour mesurer la taille des particules dans des dispersions de particules fines ou de nano particules. Chaque technique a ses propres

avantages, inconvénients et limitations selon les conditions d'application. Il est nécessaire d'analyser ces potentialités et ces contraintes en référence avec un procédé et selon les conditions de fonctionnement. Cette étude tente de faire cela en privilégiant un procédé de broyage par voie humide. La connaissance apportée par cette étude contribuera à préciser l'information sur la taille des particules du produit élaboré, ce qui permettra d'améliorer l'interprétation, le contrôle et l'optimisation selon différents angles de vue (rendement énergétique, qualité du produit, usure des billes de broyage, …) du procédé en voie humide de broyage par microbilles.

I.2 Problèmes et opportunités

La caractérisation de la taille de particules lors de la production de nanoparticules au moyen d'un procédé de broyage en voie humide est spécifique pour diverses raisons. Les paragraphes suivants décrivent la problématique particulière et les solutions qui ont été analysées dans cette étude.

- Les dispersions traitées par broyage contiennent souvent des impuretés et des additifs etc. Par exemple, pour beaucoup d'applications industrielles, des dispersions de $CaCO_3$ sont préparées à partir de $CaCO_3$ brut qui peut contenir des impuretés comme la silice ou le carbonate de magnésium. De même, lors de procédés de broyage en voie humide, il est courant dans la pratique d'ajouter des additifs dans la dispersion pour contrôler l'agrégation et la dispersibilité des particules. Or, il existe un manque de connaissances pour la caractérisation de telles dispersions. Concernant la spectroscopie acoustique, Babick et al. (2000) ont ainsi souligné le fait que seulement une petite expérience a été acquise concernant la caractérisation de la taille des particules dans des conditions réelles, c'est-à-dire en présence de contaminants, pour des systèmes multi-constituants ou pour le cas où la connaissance des phases incluses est incomplète. De même, Povey (2006) a insisté sur l'importance de la caractérisation des tensio-actifs dans le solvant pour obtenir une caractérisation fine de la taille au moyen de la spectroscopie acoustique. L'un des objectifs de cette étude est de s'attaquer à ce problème de manière à trouver les conditions adéquates dans lesquelles des dispersions contenant des impuretés peuvent être analysées par mesure de l'atténuation acoustique.
- Lors de procédés de broyage en voie humide, des dispersions de différentes concentrations peuvent être utilisées. Il est important de savoir comment la concentration de la dispersion peut influencer le procédé de broyage. La difficulté avec de nombreuses techniques de caractérisation de la taille comme la diffusion dynamique de la lumière ou la diffraction laser est qu'elles nécessitent une dilution sévère des dispersions avant l'analyse de taille. Cette étape de dilution peut changer la taille des particules par agrégation ou de-agrégation. Aussi, de telles techniques peuvent ne pas produire une information correcte de la taille des particules, ce qui peut entraîner une mauvaise interprétation pour le contrôle et l'optimisation d'un procédé. La technique de

spectroscopie acoustique apparaît comme une solution intéressante dans de telles situations. Cependant, il y a un manque de connaissance quant à l'application de cette technique pour le suivi de procédés de broyage en voie humide. Cette analyse doit être effectuée en considérant différents aspects de la caractérisation de taille réalisée avec cette technique et en comparant les résultats trouvés avec ceux obtenus par le biais d'autres méthodes. Pour parvenir à une meilleure conception des unités, un meilleur contrôle des procédés, et pour permettre l'optimisation des conditions de fonctionnement, il est nécessaire de comprendre les raisons des différences de résultats qui peuvent être observées lorsque on mesure la taille des particules en utilisant des techniques différentes. Un deuxième objectif de cette étude est donc d'analyser les effets de la concentration des dispersions sur l'analyse de taille lors de la production de particules fines par broyage en voie humide.

- La caractérisation de la taille des particules lors de la production de particules fines ou de nanoparticules est particulière par rapport à d'autres procédés dans le sens où: (i) La modification de la taille moyenne des particules, résultant de leur fragmentation, est rapide. (ii) Le degré de polydispersité dans le produit change au cours du temps. (iii) La nature des interactions entre les particules change; avant broyage les particules sont non-colloïdales, elles le deviennent après un certain temps d'opération. Ces conditions font que la caractérisation au cours d'un procédé de broyage est plus complexe que le cas d'une simple dispersion et elle nécessite de fait une étude spécifique de sorte à bien comprendre les détails de cette opération selon différents aspects.
- Il y a un manque de connaissances pour comprendre comment la qualité du produit broyé final est affectée lors du broyage dans des broyeurs à billes agités. Dans cette étude nous explorons plusieurs aspects de la caractérisation de taille, ainsi que quelques autres paramètres opératoires qui peuvent influencer la qualité du produit broyé.

I.3 Objectifs de l'étude

L'objectif principal de cette thèse est d'analyser les potentialités, les limitations et les problèmes rencontrés dans la mesure de taille de particules en considérant la spectroscopie acoustique, la diffusion dynamique de la lumière et la diffraction laser lors de la production de particules fines ou de nanoparticules en suspension au moyen d'un procédé de broyage en voie humide. En particulier, nous souhaitons analyser:

- Les effets des impuretés sur la caractérisation de la taille par spectroscopie acoustique dans l'intention de trouver les conditions adéquates pour lesquelles cette technique peut s'appliquer lors de procédés de broyage en voie humide en présence d'impuretés et/ou d'additifs.

- Les effets de la concentration des dispersions sur la mesure de taille lors de la production de particules fines par un procédé de broyage en voie humide. En particulier, nous envisageons de comparer les résultats de la mesure de taille par différentes techniques et d'expliquer les raisons qui conduisent à l'obtention de résultats différents.
- Les effets de la caractérisation de la taille, ainsi que ceux de différents paramètres opératoires sur la qualité du produit broyé dans un broyeur à billes agité.

I.4 Structure de la thèse

L'étude a été entreprise selon différentes phases qui sont discutées lors des différents chapitres de la thèse.

Chapitre I: Ce chapitre constitue l'introduction de la thèse. Le contexte, les motivations, la problématique traitée et les objectifs du travail sont précisés. De même, la structure de la thèse et la définition de quelques termes ou terminologies importants sont donnés dans cette partie. Ce chapitre donne un aperçu de l'originalité, de la contribution et de l'innovation du travail proposé. Il explique comment et sur quels aspects cette étude est différente d'autres travaux dans le domaine.

Chapitre II: Ce chapitre rapporte différents aspects de la littérature qui sont en relation avec le domaine abordé dans la thèse. Il présente les aspects théoriques, ainsi les développements et les applications pratiques associées aux différentes techniques de caractérisation de la taille. Il dresse également un état de l'art sur les procédés de broyage en voie humide et sur la stabilité des suspensions colloïdales. Ces éléments sont importants pour situer le contexte de la thèse.

Chapitre III: Le troisième chapitre décrit la méthodologie utilisée dans ce travail. Les méthodes, les matériaux et les équipements principaux sont détaillés. Quelques résultats préliminaires importants sont également présentés dans cette partie.

Chapitre IV: Dans les procédés de broyage en voie humide, les dispersions traitées contiennent souvent des additifs ou des impuretés. Ce chapitre analyse les effets des impuretés sur la caractérisation de la taille des particules par spectroscopie acoustique. Les résultats présentés dans ce chapitre constituent donc une base pour l'analyse de la caractérisation de la taille de particules en suspension en présence d'additifs ou d'impuretés lors de procédés de broyage en voie humide. Le travail présenté dans ce chapitre a fait l'objet d'une publication dans la revue Journal of Powder Technology. Nous présentons dans ce chapitre le contenu de l'article sans modification. Toutefois, à la fin du manuscrit, quelques résultats complémentaires sont donnés dans les annexes A, B, C et D.

Chapitre V: Dans le cinquième chapitre nous analysons les effets de la concentration des dispersions sur la caractérisation de la taille au cours de la production de particules fines dans un broyeur à billes

agité en utilisant les techniques de la spectroscopie acoustique et de la diffusion dynamique de la lumière**.** Dans ce chapitre nous comparons et nous avançons des hypothèses pour expliquer les différences de résultats entre les deux techniques. Le travail présenté dans ce chapitre a également été accepté pour publication dans une Journal of Powder Technology. Nous présentons le contenu de l'article sans modification par rapport à la version de l'article mais des résultats complémentaires qui nous ont servi à l'élaboration de la publication ont été rajoutés à la fin du manuscrit dans l'annexe E..

Chapitre V I: Le chapitre VI a trait à la discussion des effets de la caractérisation de taille et de quelques paramètres sur la qualité du produit obtenu par broyage en voie humide. Ce chapitre a aussi été présenté sous la forme d'un article qui a été accepté et présenté lors d'une communication orale dans le congrès "The World Congress on Particle Technology" en avril 2010 à Nuremberg en Allemagne.

Chapitre VII: Enfin, le chapitre VII donne les conclusions et les perspectives de ce travail de thèse.

I. Introduction

I.1 Context and motivation

The demand for dispersions of fine and nano particles is increasing day by day. They have wide applications in many areas such as paints, pigments, paper coatings, adhesives, catalysts, absorbent materials, fillers, printing inks, carbonless copying papers, emulsions, micro emulsions, ointments, ceramics, cement, fiber, reinforcement of plastics, dairy products, water proofing materials, cleansing agents and cosmetics etc. Fine and nano particles, due to small size and high surface area-to-volume ratios, exhibit physicochemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. They, generally, result in improvement of homogeneity, solubility, rheological properties, strength and reactivity etc. of the products formed with them.

There are two approaches for production of fine and nano particles: (i) bottom-up (in which fine and nano particles may be produced by a reaction, condensation or aggregation of molecules etc.) and (ii) top-down (in which fine and nano particles may be produced by physical processes such as grinding). This study is related to top-down approach. In top down approach, wet grinding and dry grinding are two possible options. This study takes into consideration the wet grinding process for production of fine and nano particles. The stirred media milling, that is a prospective technology in the domain of wet grinding because of many advantages such as relative low agglomeration tendency, low material losses, less possibility of oxidation, easy handling of toxic materials, elimination of need of employing a device for air cleaning, elimination of the problem of dust explosion and better heat transfer options, has been focused in this study.

In process of production of fine and nano particles, the particle sizing plays an important role. In the recent past, many modern techniques of particle sizing have been developed for the dispersions of fine and nano particles. Each technique has its own advantages, disadvantages and complications depending upon conditions of the application. There is a need to understand the potentials, limitations and complications of particle sizing techniques with reference to the processes and conditions of applications. This study attempts this by focusing on the wet grinding process. The knowledge obtained by this study will contribute in precising information of particle size of the product that will be helpful in improving the interpretation, control and optimization of various aspects of the wet grinding process.

I.2 Problems and opportunities

The particle sizing in production of fine and nanoparticles by means of wet grinding process is typical in many senses. The following paragraphs describe the typical problems and opportunities that have been addressed in this study.

- The dispersions during wet grinding involve often impurities and additives etc. For example, in many industrial applications, dispersion of $CaCO_3$ are prepared from raw $CaCO_3$ that may contain impurities such as silica or $MgCO_3$. Similarly, during wet grinding processes, it is a common practice to add additive(s) in the dispersion to control aggregation and dispersity of the particles. For particle sizing of such dispersions, there exists a lack of knowledge. It is less known how to treat particle sizing of such dispersions. Pointing out this lack, Franck Babick et al. (2000) write that only little experience has been gained in particle sizing under more real conditions, e.g. for the presence of contamination, for multi-component-systems or for the case that the knowledge of the involved phases is incomplete . Similarly, Povey (2006) has emphasized the importance of characterizing the surfactants in the solvent for successful particle sizing by means of acoustic attenuation spectroscopy. One of the objectives of this study is to the address this problem in order to find possible conditions in which dispersions with impurities may be studied by means of acoustic attenuation spectroscopy.

- During wet grinding process, dispersions of different concentrations may be used. It is important to understand how different concentrations of the dispersions influence the grinding process. The problem with many techniques of particle sizing such as dynamic light scattering and laser diffraction technique is that they require the sample to be diluted before particle sizing. This step of dilution may change size of the particles by aggregation or de-aggregation. Thus, such techniques may not generate the right information of particle size that is important to interpret, control and optimize a process. The technique of acoustic attenuation spectroscopy is considered as a solution in such cases. However, there exists a lack of comprehensive studies on application of this technique into wet grinding process that take into consideration different aspects of particle sizing carried out with this technique with an emphasis on comparison of its results with the results obtained with other techniques. For a better control, designing, interpretation and optimization of a wet grinding process, it is inevitable to understand the reasons of differences in the results of particle sizing obtained through different techniques. One of the objectives of this study is to investigate the effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process.

- The particle sizing in production of fine and nanoparticles is typical from particle sizing in other processes in the senses: (i) The change in average particle size of the product is rapid due to relatively fast breakage of particles. (ii) The degree of poly dispersity in product changes with

grinding time. (iii) The nature of interaction between particles is non-colloidal before grinding process; this interaction becomes colloidal after a certain grinding time. These conditions distinguish particle sizing in wet grinding process from particle sizing in case of simple dispersions and hence require a comprehensive study in order to understand the details of various aspects. In our work, we have addressed these issues.

- There is a lack of knowledge to understand how quality of final ground product is influenced in stirred media milling. In this study we explore various aspects of particle sizing and some other operating parameters that may influence quality of the product.

I.3 Objectives of the study

The main objective of this study is to investigate the potentials, limitations and complications in process of particle sizing considering acoustic attenuation spectroscopy, dynamic light scattering and laser diffraction technique during production of fine and nanoparticles by means of wet grinding process. In particular, we aim to investigate:

- Effects of impurities on particle sizing by acoustic attenuation spectroscopy with the intention to find the possible ways in which the technique may be applied to wet grinding processes that involve impurities and additives.
- Effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process. Especially, we aim to compare the results of particle sizing of different techniques with the goal to find the reasons of differences in the results obtained through different techniques.
- Effects of particle sizing and other operating parameters on product quality in stirred media milling.

I.4 Structure of the thesis

The study was carried out in different phases that have been discussed into different chapters of this thesis.

Chapter I: This chapter introduces this thesis. The context, motivation, problems and opportunities, objectives, important terms and terminologies, and structure of the thesis have been presented in this chapter. This chapter provides an insight into originality, contribution and innovation of the work. It has been explained how and in which aspects this study is different from other studies.

Chapter II: This chapter reviews different aspects of the literature that are related to this thesis. The theory, developments, approaches in applications and critics in particle sizing techniques, wet grinding process and colloidal stability have been thoroughly reviewed in this chapter. This chapter is important to understand the context of the work.

Chapter III: This chapter describes the research methodology adopted in this work. The chapter discusses the details of methods, materials and main equipments employed in this study. Some important results of our preliminary work are equally part of this chapter.

Chapter IV: The dispersions in wet grinding process often involve additives and impurities. This chapter analyses the effects of impurities on particle sizing by acoustic attenuation spectroscopy. The results presented in this chapter provide the basis for studying the particle sizing of dispersion with additives and impurities in wet grinding process. The work presented in this chapter has already been published in the journal of Powder Technology. We present the paper in this chapter without any technical changes. The supplementary results, however, are given in appendices A, B, C and D at the end of the manuscript.

Chapter V: This chapter investigates the effects of concentration of dispersions on particle sizing during production of fine particles in a stirred media mill using the techniques of acoustic attenuation spectroscopy and dynamic light scattering. The chapter compares and investigates the differences in the results of two techniques. The work presented in this chapter has already been reviewed and accepted for publication in the journal of Powder Technology. We present the paper in this chapter without any technical changes in the text. . The supplementary results, however, are given in appendix E at the end of the manuscript.

Chapter VI: This chapter discusses the effects of particle sizing and operating parameters on product quality in wet grinding process. This research work has been orally presented in an international conference “The World Congress on Particle Technology” held on 26-29 April 2010 in Nuremberg, Germany.

Chapter VII: This is the final chapter of this thesis and summarizes the conclusions drawn from this study. The work that may be undertaken by prospective researchers has been highlighted equally in this chapter.

I.5 Important terms and terminologies

Basic terms and terminologies that are important to understand theme of the study are introduced below.

Dispersion: It is a finely distributed mixture of two or more insoluble (or slightly soluble) phases into each other.

Disperse medium: It is the component of a dispersion that is lower in quantity. It is also known as dispersed medium, internal medium or discontinuous medium. The word of “phase” is equally used as an alternative to the word of “medium”.

Dispersion medium: It is the component of a dispersion that is higher in quantity. It is also known as dispersion medium, external medium or continuous medium. The word of “phase” is equally used as an alternative to the word of “medium”.

Particle: It is defined as a small object that behaves as a whole unit in terms of its transport and properties.

Fine particle: A particle that has at least one dimension in the range of 100 to 2500 nm.

Nano particle: A particle that has at least one dimension in the range of 1 to 100 nm.

Colloidal particle: A particle that has at least one dimension in the range of 1 to 1000 nm.

Colloid: A dispersion that involves colloidal particles is termed as colloid or colloidal dispersion.

Aggregation: A process by which particles collect to form a cohesive mass or cluster, the resulting structure is called aggregate.

De-aggregation: It is inverse process of the aggregation.

Wet grinding process: The grinding process in which grinding material is treated in liquid phase.

Suspension: It is the dispersion formed by dispersing the solid particles in a liquid.

I.6 References

Babick F., Frank H., Ripperger S., Dependence of ultrasonic attenuation on the material properties, Colloids and Surfaces A, 172 (2000) 33-46.

Povey M. J. W., Acoustic methods for particle characterization, KONA, 24 (2006) 126-133.

As per requirements of the university, a preface in the beginning and concluding remarks at the end of the chapter have been given in French.

Préface en français

Avant de présenter le travail que nous avons mené dans le cadre de cette thèse, nous allons rappeler dans ce chapitre quelques éléments importants pour situer le contexte scientifique de l'étude.

Comme nous l'avons précisé en introduction, les dispersions solide-liquide traitées par broyage humide sont généralement des systèmes concentrés, contenant des impuretés ou des additifs et qui sous l'effet des forces mécaniques appliquées subissent des modifications de distribution de taille importantes. Les opérations de broyage ultrafin ou de nanobroyage permettent même l'obtention de particules colloïdales. Dans les milieux colloïdaux, les forces s'exerçant entre les particules conditionnent l'état de dispersion des suspensions. Au cours des procédés de broyage, il n'est pas rare que des additifs soient ajoutés aux suspensions traitées pendant ou après l'opération pour éviter la re-agrégation des fragments fins produits et assurer la stabilité des suspensions broyées. Aussi, dans une première partie, nous rappellerons les principales forces attractives et répulsives s'exerçant dans les milieux colloïdaux et nous évoquerons les méthodes usuelles permettant de garantir la stabilité des suspensions broyées.

Dans une deuxième partie, nous donnerons quelques généralités sur les techniques optiques et acoustiques que nous avons utilisées pour la caractérisation de la taille de particules en suspension. Nous développerons notamment les techniques par diffraction laser et par diffusion dynamique de la lumière, ainsi que la technique acoustique basée sur la mesure de l'atténuation d'une onde sonore. Enfin, la dernière partie de ce chapitre sera consacrée au procédé de broyage en voie humide et plus particulièrement aux procédés reposant sur la technologie des broyeurs à billes agités qui feront l'objet des chapitres V et VI.

II. Literature Review

A particle that has a linear dimension in the range 1nm to 1 μm is termed as colloidal particle and a dispersion of such particles is called a colloidal dispersion or a colloid (Schramm, 2004, Lagaly, 2005). Colloidal dispersions have wide applications in many areas such as paints, pigments, paper coatings, adhesives, catalysts, absorbent materials, fillers, printing inks, carbonless copying papers, emulsions, micro emulsions, ointments, ceramics, cement, fiber, reinforcement of plastics, dairy products, water proofing materials, cleansing agents and cosmetics etc. Colloidal particles, due to small size and high surface area-to-volume ratios, exhibit physicochemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. This study deals with applications of particle sizing techniques in production of dispersions of fine and nano particles (colloidal dispersions) by means of wet grinding process. This chapter reviews three important issues addressed in this study: colloidal stability, particle sizing of colloids and production of colloids by means of wet grinding process.

II.1 Colloidal stability

II.1.1 Surface forces between colloidal particles

There exist many repulsive and attractive forces between colloidal particles and their mutual interaction play an important role in determining colloidal stability (Schramm 2004). In different studies, these forces have been termed differently leading to bit confusion. This is, probably, due to different context, nature of application or different names of contributing scientists etc.

II.1.1.1 London-van der waals forces

These are due to interaction between two dipoles which are either permanent or induced. In some cases, if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. In the literature, many methods and approaches have been proposed in order to measure such forces. For example, Bown and Jenner (1995), Dzyaloshinskii et al. (1961), Hough and White (1980) and Niham and Parsegian (1997) have discussed different methods to calculate the London-van der Waals interaction energy. These methods may broadly be classified into: (1) microscopic approaches and (2) macroscopic approaches.

In a microscopic approach, the work of London (1930) and Wang (1927), Margenau (1931), Hamaker (1937) and de Boer (1936) are important. In these studies, the Hamaker's approach is not only easy in

understanding but also that it works over a wider range (Liang et al., 2007). He considered spherical bodies, assumed pairwise additivity of interatomic dispersion energies, and demonstrated the essential results that although the range of atomic forces was of the order of atomic dimensions, the sum of the dispersion energies resulted in an interaction range for colloidal bodies of the order of their dimensions (Liang et al., 2007). For two spheres of equal radius, *a*, at a surface to surface separation distance, *D*, apart along the centre to centre axis, the total interaction energy, V_A, is given by:

$$V_A(D) = -\frac{A_H}{6}\left[\frac{2a^2}{D^2+4aD} + \frac{2a^2}{(D+2a)^2} + \ln\left(1-\frac{4a^2}{(D+2a)^2}\right)\right] \qquad \ldots\ldots (2.1)$$

If the Hamaker constant (A_H) is known, it is possible to calculate the interaction energy between the particles provided that the particle radius (a) and interparticle distance (D) are known. In a macroscopic approach, the problem of additivity is completely avoided in the Lifshitz theory (1956). In this theory, atomic structure is neglected and large bodies are treated as continuous media and forces are derived in terms of the bulk properties such as dielectric constants and refractive indices (Liang et al. 2007). However, all the aforementioned equations for the interaction energies remain valid even within the framework of continuum theories. The difference is that the Hamaker constant is to be calculated in a different way. The details on the techniques to calculate Hamaker constant under a range of situations may be studies in the work of Gregory (1970), Hom (1981), Israelachvili (1972), Mahanty and Ninham (1976), Prieve and Russel (1988). Knowing the interaction energy (V_A) and surface to surface separation distance between two spheres of equal radius (D), the attractive force (F_A) may be calculated as:

$$F_A = -\frac{\mathrm{d}V_A}{\mathrm{d}D} \qquad \ldots\ldots (2.2)$$

The literature review explains that despite availability of aforementioned equations, the determination of exact interaction energy is complicated. Hamaker constant may be influenced by number of factors such as retardation effect. Mahanty and Ninham (1976) have discussed some of such cases in detail.

II.1.1.2 Electrical double layer forces

Colloidal particles dispersed in water and any liquid of high dielectric constant usually develop a surface charge. Israelachvili (1992) discusses that the charging of a surface in a liquid can be brought about in two charging mechanisms: (i) by the ionization or dissociation of surface groups, which leaves behind a charged surface (e.g., the dissociation of protons from carboxylic groups, which leaves behind a negatively charged surface) and (ii) by the adsorption (binding) of ions from solution onto a previously uncharged surface. The adsorption of ions from solution can also occur onto oppositely charged sites, also known as ion exchange. Liang et al. (2007) explain that electrical neutrality of the system implies that the dispersing medium must contain an equivalent charge of the opposite sign. These charges are carried by ions, i.e., by an excess of ions of one sign on the particle surface and an

excess of ions of the opposite sign in the solution. If we consider an individual particle immersed in the liquid, it is surrounded by an electric double layer. One of this double layer is formed by the charge in the surface of the particles. Another layer of the electrical double layer is formed by the excess of oppositely charged ions in the solution. As a result of their thermal motion the electric charge carried by this layer extends over a certain distance from the particle surface, and dies out gradually with increasing distance (diffuse layer) into the bulk liquid phase. Bell et al. (1970), Gregory (1975), Hogg and Healey (1966), Ohshima and Kondo (1988), Kar and Chander (1973) discuss the different means of determining sphere-sphere double layer interaction energy in detail. However, the work of Bell et al. (1970) that is based upon linear superposition approximation (LSA) provides a simple expression for determining sphere-sphere double layer interaction energy as below:

$$V_R = \frac{128\pi a_1 a_2 n_\infty kT}{(a_1 + a_2)\kappa^2}\gamma_1\gamma_2 \exp(-kh) \qquad \ldots\ldots (2.3)$$

Where, h is the surface-surface separation between the particles, a the particle radius of different sizes, κ the Debye–Hückel parameter, n_∞ the bulk density of ions and γ the reduced surface potential

$$\gamma = \tanh\left(\frac{ze\psi}{4kT}\right) \qquad \ldots\ldots (2.4)$$

The above equation is valid when both the conditions $\kappa a > 5$ and $h << a$ are satisfied.

II.1.1.3 Steric forces

Steric forces between polymer-covered surfaces or in solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive depletion force between them. Theories of steric interaction are not well developed (Liang et al., 2007). However, the work of de Gennes (1987) and Milner et al. (1988) explain that the magnitude of the force between surfaces coated with polymers depends on three important factors:

- The quantity or coverage of polymer on each surface.
- On whether the polymer is simply adsorbed from solution (a reversible process) or irreversibly grafted onto the surfaces.
- On the nature of the solvent.

Liang et al. (2007) explain that different components contribute to the force, and which component dominates the total force is situation specific.

II.1.1.4 Non-DLVO forces

The literature review explains when two surfaces or particles approach closer than a few nanometer, the London-van der Waals attractive forces and electric double layer repulsive forces are no longer able to explain the stability of the particles in a dispersion indicating the presence of some forces that are different from London-van der Waals attractive forces and electric double layer repulsive forces. Liang et al. (2007) point out that theories of van der Waals and double layer forces fail to explain the matter of stability of dispersions at a distance of few nanometers because both theories have been developed on the basis of the bulk properties of the intervening solvent such as its refractive index, dielectric constant and density; and in both theories the individual nature of the molecules involved, such as their discrete size, shape, and chemistry has not been taken into consideration. The literature review explains that the additional forces can be monotonically repulsive, monotonically attractive, or even oscillatory in some cases. These additional forces are often named as non-DLVO forces in the literature. Bergeron (1999) and Ninham (1999) state that physical origin of the forces is still obscure.

Churaev and Derjaguin (1985) and Leikin (1993) consider Hydration force as an important and one of the most widely studied but controversial non-DLVO force. It is a strong short-range force that decays exponentially with the distance, *D*, between the surfaces.

$$F_{\mathrm{SOL}}(D) = Ke^{-D/l} \qquad \ldots\ldots (2.5)$$

Where $K>0$ relates to the hydrophilic repulsion forces and $K<0$ to the hydrophobic attraction forces and l is the correlation length of the orientational ordering of water molecules. The physical mechanisms underlying the hydration force are still a matter of debate. One possible mechanism is the anomalous polarization of water near the interfaces, which completely alters its dielectric response (Marčelja, 1997; Ruckenstein and Manciu, 2002; Leikin and Kornyshev, 1990). On the other hand, computer simulations show that water has an anomalous dielectric behavior near charged interfaces (Faraudo and Bresme, 2004), but the observed electrostatic fields clearly differ from the predictions of electrostatic theories on hydration forces (Ruckenstein and Manciu, 2002; Gruen and Marčelja 1983). The effect of this anomalous dielectric behavior of water on the electrostatic force between surfaces or interfaces is still ambiguous.

II.1.1.5 Hydrophobic forces

At long-range (>10 nm) attractive force operates between hydrophobic surfaces immersed in water and aqueous solutions (Israelachvili and Pashley, 1982). Liang et al. (2007) discuss that so far no generally accepted theory has been developed for these forces. However, Israelachvili (1992) is of the view that hydrophobic force arise from overlapping solvation zones as two hydrophobic species come together. Eriksson et al. (1989) have used a square gradient variational approach to show that the mean field theory of repulsive hydration forces can be modified to account for some aspects of hydrophobic

attraction. On the other hand, Ruckenstein and Churaev (1991) propose a completely different origin that attributes the attraction to the coalescence of vacuum gaps at the hydrophobic surfaces. The exact origins and character of the hydrophobic attraction still remain an open question in the literature.

II.1.2 Electrostatic stabilization (DLVO theory)

DVLO theory, contributed by Deryaguin and Landau (1941) and Verwey and Overbeek (1948), describe electrostatic stabilization at fundamental level. It considers van der Waals attraction and double-layer repulsion in order to establish an energy-distance curve to describe the conditions of stability or instability.

Attractive energy: The attractive energy G_a between two individual atoms or molecules is given by:

$$G_a = -\frac{\beta_{11}}{r^6} \qquad \ldots\ldots (2.6)$$

Where, β_{11} is a constant that refers to identical atoms or molecules whereas, r is interatomic distance. The individual contributions of atoms or molecules may be compounded for colloidal particles composed of assemblies of molecules or atoms. Such assemblies show no net dipole moment because of overall cancellation of Keesom and Debye forces (vectors). Therefore, only London interaction is taken into consideration. For two equal colloidal particles, each of radius R and at a distance h in vacuum, Van der Waals energy of attraction, G_A, is given by:

$$G_A = -\frac{A_{11}}{6}\left[\frac{2}{s^2-4}+\frac{2}{s^2}+\left(\frac{s^2-4}{s^2}\right)\right] \qquad \ldots\ldots (2.7)$$

Where A_{11} is Hamaker constant and given by: $A_{11} = \pi\, q^2\, \beta_{11}$, q represents number of atoms or molecules per unit volume and $s = (2R+h)/R$. For very short distance of separation between colloidal particles when $h << R$, the above expressions may be approximated as:

$$G_A = -\frac{RA_{11}}{12h} \qquad \ldots\ldots (2.8)$$

In presence of a medium (solvent), the Hamaker constant A_{12} of material 1 dispersed in a medium of Hamaker constant A_{22} is given as:

$$A_{12} = A_{11} + A_{22} - 2A_{12} = \left(A_{11}^{1/2} - A_{22}^{1/2}\right)^2 \qquad \ldots\ldots (2.9)$$

In most disperse system, $A_{11} > A_{22}$ resulting in positive values of A_{12} indicating attraction between the particles.

Energy of repulsion: In a diffused double layer, the potential at the surfaces Ψ_0 reduces linearly to a value Ψ_d (located at the canter of the specifically absorbed negative ions) and then exponentially with

decrease in distance *x*, approaching zero in bulk solutions. Double layer thickness (*1/κ*) may be presented by reciprocal of Debye-Huckel parameter (*K*):

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_r \varepsilon_0 kT}{2n_0 Z^2 e^2} \right)^{1/2} \quad \ldots\ldots (2.10)$$

Where, ε_r is relative permittivity, ε_0 permittivity of free space, *k* Boltzmann constant, *T* absolute temperature, n_0 number of ions of each sort in the bulk phase, *Z* the valency of ions and *e* the electronic charge. Let the distance between two same particles in dispersion be *h*. In the cases when $h > 2/\kappa$, two double layers can be developed them without restriction leading to zero stern or surface potential at the mid point between the particles. However, in the case when $h < 2/\kappa$ the situation is different, there appears a potential at the mid-distance between the particles leading to repulsion between the particles. Tadros (2006) explains that energy of repulsion, G_{el} may be presented by the following expression which is valid for $\kappa R<3$.

$$G_{el} = \frac{4\pi\varepsilon_r \varepsilon_0 R^2 \psi_d^{\,2} \exp(-\kappa h)}{2R + h} \quad \ldots\ldots (2.11)$$

Where, ε_r represents relative permittivity, ε_0 permittivity of free space, *R* radius of each particle, Ψ_d surface potential, *K* Debye-Huckel parameter and *h* distance between two particles. The expression explains that G_{el} decreases exponentially with increase of distance between particles (*h*). At higher values of *h*, G_{el} tends to zero. At any given *h*, G_{el} increases with increase in thickness of double layer (*1/κ*) which ultimately depends upon concentration of electrolyte and valency of ions. The conclusions from the discussion, based on figure II.1, are summarized in table II.1. Tadros (2006) discusses that for stability of colloidal dispersion the value of G_{max} must be larger than thermal energy (*kT*) of the particles. Generally, $G_{max} > 25kT$ is an adequate condition for colloidal stability. G_{max} particularly depends upon on surface (stern or zeta) potential, electrolytes concentration and valency.

Table II.1: Electrostatic stabilization – conclusions from energy-distance curve

- Double Layer Repulsion (G_{el}) decreases exponentially with increase in h tending to zero at large distance (*h*) between particles.
- Waals energy of attraction (G_A) also decreases with increase in h but not tending to zero at large distance (*h*) between particles.
- G_T *vs. h* curve shows two minima (Primary minimum (G_{min1}) and Secondary minimum (G_{min2})) and one maximum (G_{max}).
- G_{max} refers to a state in which maximum net Double Layer Repulsion (G_{el}) is present into the system. It is referred as energy barrier also.

Tadros (2006) discussing the example of an electrolyte of monovalent ions and cations, describes that conditions of stability ($G_{max} > 25kT$) may be achieved by having a high zeta potential (>40*mV*) and low electrolyte concentration (< 10-2 mol/dm^3). Tadros (2006) as in figure II.2 demonstrates how G_{max} gradually decreases and eventually approaches to zero at a critical electrolyte concentration for 1:1

electrolyte. The increase in the valency of electrolyte at any given concentration of electrolyte causes decrease in G_{max} leading to poor stability.

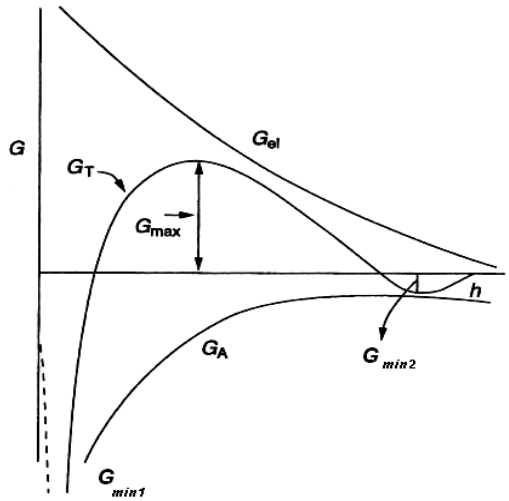


Fig. II.1

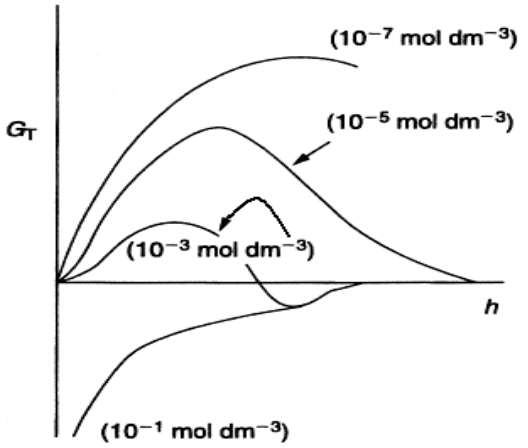


Fig. II.2

Fig. II.1: Variation of G_{el}, G_A and G_T with h (distance between two particles).
Fig. II.2: Variation G_{max} with concentration of electrolyte.

II.1.3 Steric stabilization

Steric stabilization is a generic term that embraces all aspects of colloidal stabilization by non-ionic macromolecules (Overbeek 1997). Tadros (2006) expresses that steric stabilization arises from the presence of adsorbed or grafted surfactant or polymer layers, mostly of the non-ionic type, creating repulsion between the particles. Lagaly (2005) describes when two particles with their organic chains come closer; the chains lose conformational entropy in the gap between the particles leading to volume restriction effect or entropic stabilization that ultimately results in a resistance between the particles as shown in figure II.3 (a). Taking on another possibility of steric stabilization, Lagaly (2005) emphasizes that in all cases there is a strong possibility of a local increase in concentration of organic material between the particles (mentioned by region of dotted lines in figure II.3 (b)) that may create an osmotic effect resulting in repulsive force between the particles causing stability. The pragmatic formulae may be employed for calculating the interaction energy due to steric stabilization (Vincent et al., 1986). Generally, it is difficult to find the correct input data such as the segment density distribution of the macromolecules or the contour length of the macromolecular envelope (Lagaly, 2005). He further expresses that in some colloidal systems especially in biological ones, a combination of electrostatic and steric stabilization occurs when particles carry surface charges or when the adherent macromolecules are polycations or polyanions as shown in figures II.3 (c), and figure II.3 (d).

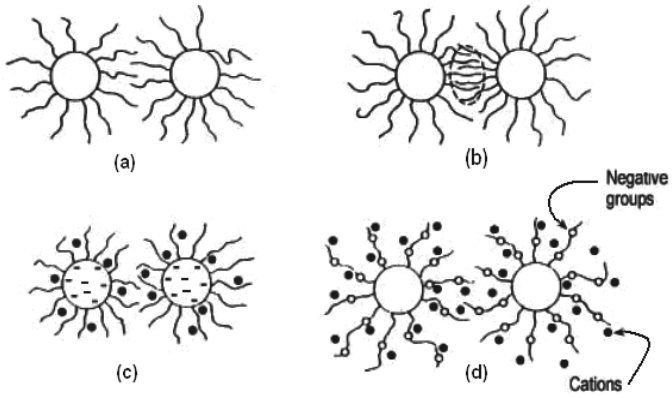


Fig. II.3: Different patterns of steric stabilization.

Table II.2 summarizes the important requirements for steric stabilization (Lagaly, 2005):

Table II.2: Steric stabilization – summary of important requirements

i- Steric stabilization requires threshold concentrations of polymers.
ii- The absorbed polymers which are higher in molecular mass need lower amounts for stabilization.
iii- The macromolecules should be strongly bound on the surface.
iv- The interaction between polymer and solvent is quite important in steric stabilization. Stabilization increases with the quality of the solvent. In a good solvent, interpenetration of the chains is disfavored, promoting stabilization. On the other hand, interpenetration is thermodynamically favored in a worse-than-θ solvent, and the dispersion is destabilized.
v- The system becomes unstable under θ conditions within a narrow temperature range.
vi- Steric stabilization may be favored or disfavored by temperature depending on other conditions.
vii- In many cases, destabilization may only be obtained by changing the temperature or the quality of the solvent.
viii- Destabilization is reversible in general; change in temperature or the quality of the solvent leads to re-dispersion and stabilization.

II.1.4 Comparison: steric stabilization vs. electrostatic stabilization

Steric stabilization has many advantages over electrostatic stabilization (Napper, 1983) e.g.:

- Steric stabilization is relatively insensitive to the presence of electrolyte. For example, a dispersion stabilized by 1:1 electrolytes will not be stable and coagulate when the concentration of electrolytes exceeds the 10^{-1} M. Generally, dispersions with steric stability have not such limitations because the dimensions of polymer chains display no such dramatic sensitivity.

- Electrostatic stabilization is less effective in non-aqueous dispersion media as compared to aqueous media because of the low relative dielectric constant (<10) of most of the non-aqueous media. Steric stabilization is effective in both non-aqueous media and aqueous media.

- In electrostatic stabilization in non-aqueous media, the thickness of the double layers may grow so large, (due to the low dielectric constant of the dispersion medium), that the mere preparation of high solids dispersions forces the particles to approach closer resulting in coagulation. In aqueous dispersion media, the preparation of charge-stabilized particles at high solids dispersions is often

difficult because of the gel formation induced by the interactions between the double layers surrounding each particle.

- In case of electrostatic stabilization, if coagulation of particles is induced by the addition of electrolyte, it remains irreversible on subsequent dilution. In contrast, flocculation of sterically stabilized dispersions (induced by the addition of a non-solvent for the stabilizing moieties) can usually be reversed spontaneously by mere dilution of the non-solvent concentration to a suitably low value. It points out that sterically stabilized dispersions may be thermodynamically stable while charge stabilized dispersions are only thermodynamically metastable. As a result, for charge stabilized dispersions, the coagulated state represents a lower energy state and the coagulation can be reversed only after input of work into the system. Another important consequence of the thermodynamic stability of sterically stabilized dispersions is that they may redisperse spontaneously after drying.

II.1.5 Summing up - colloidal stability

The process of grinding is characterized by rapid change in particle size with increasing grinding time. The measurements of interacting forces, in such cases, to determine stability is not feasible. Many indirect approaches have been reported in the literature in order to estimate stability of the colloidal systems. One of very frequently used method in many studies is the measurement of the zeta potential which provides an indication of the potential stability of the colloidal system. In general, but not essentially, the dividing line between an aqueous particle dispersion being stable and not being stable is considered to be +30mV or -30 mV. Literature review indicates that three factors may, significantly, affect zeta potential:

- Changes in the pH of the sample.
- The conductivity of the medium (i.e. concentration and type of the salt).
- The type and concentration of an additive in the product.

The manipulation of these factors may lead to control of desirable zeta potential of the system. In a grinding process, the breakage of particles yields smaller particles resulting in overall increase in surface area of the product for which the mechanism of interaction between surface forces may change. Literature review explains, in grinding experiments when colloidal stability is achieved by means of electrostatic stabilization, the common approach to control zeta potential is the control of pH value. An already developed study of zeta potential versus pH may be useful. The studies such as of Breitung-Faes and Kwade (2008) and Stenger et al. (2005) demonstrate application of this approach, in acquisition of stability by electrostatic means. In the literature, many studies report acquisition of stability by steric stabilization for which appropriate additives are mixed in the dispersions. For example, in a study on an organic pigment (Magenta 122), Bilgil et al. (2006) use Sodium N-methyl-

oleyl taurate (OMT) as a dispersing additive. In another study on rheological behavior an granulometric properties of dense aggregated suspensions of $CaCO_3$ in an ultrafine grinding process, Garcia et al. (2003) use sodium polyacrylate in order to achieve steric stabilization in the grinding process. In another related paper, Garcia et al. (2004) compare the results of grinding experiments in presence and in absence of additives. Furthermore, their work takes into consideration the effects of different proportions of a dispersing additive (sodium polyacrylate) on grinding results. In our work, we consider steric stabilization using sodium polyacrylate following the work of Garcia et al. The full details of the work of Garcia et al. may be consulted in his PhD dissertation (Garcia, 2000).

Another example of indirect methods to study the stability is to study the aggregation process in a colloidal system which may be carried with suitable particle sizing equipments. In this regard, the work of Tourbin and Frances (2009) on monitoring of the aggregation process of dense colloidal silica suspensions in a stirred tank by acoustic spectroscopy may be consulted. Similarly, in another work, the matter of stability has been studied by Tourbin and Frances (2007) in colloidal silica by taking the turbidity of the colloidal system into consideration.

II.2 Particle sizing of colloidal dispersions

The review on particle sizing techniques explains that there exist number of particle sizing methods and techniques which vary in terms of principal of technique, way of application, range of particle size, time of measurement, concentration of the sample, type of particle size distribution etc. The literature review explains that laser diffraction technique, dynamic light scattering and acoustic attenuation spectroscopy are frequently used particle sizing techniques for colloidal dispersions especially in wet grinding processes.

II.2.1 Laser diffraction technique

The literature review shows that development of the laser diffraction technique for particle sizing began around 1970 (Ma et al., 2000). Early publications on laser diffraction technique for particle sizing came from Cornillault (1972), McSweeney and Rivers (1972) and Swithenbank et al (1977). Laser diffraction technique is based on the principle that particles passing through a laser beam will scatter light at an angle that is directly related to their size (Ma et al., 2000; Cornillault, 1972; Swithenbank, 1977; Black et al. 1996; Keck and Muller, 2008). As particle size decreases, the observed scattering angle increases logarithmically. The observed scattering intensity is also dependent on particle size and diminishes, to a good approximation, in relation to the particle's cross-sectional area. Large particles, therefore, scatter light at narrow angles with high intensity whereas small particles scatter at wider angles but with low intensity. The primary measurement that has to be carried out within a laser diffraction system is the capture of the light scattering data from the particles under study. Keck (2008) expresses that laser after interacting a particle is not only diffracted but also:

i- Reflected (abrupt change in the direction of a wave front at an interface between two dissimilar media, e.g. wave front returns into the medium from which it originated),

ii- Refracted (bending of light due to a change in its speed),

iii- Absorbed (transfer of energy carried by light waves to particles) and

iv- Re-radiated (as heat or light).

Keck (2008) explains that term of scattering in fact, represents all phenomena taken together. Different scattering patterns have been shown in figure II.4.

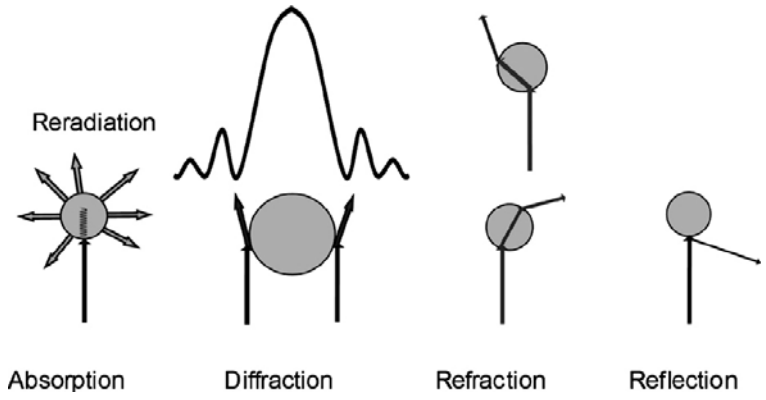


Fig. II.4: Different forms of scattering of laser.

The main parts of a laser diffraction instrument, as defined by standard of (ISO 13320-1:1999) have been summarized in table II.3:

Table II.3: Summary - important parts of a laser diffraction instrument

i. A light source (usually a laser) and a beam processing unit (usually a beam expander with integrated filter) to generate a monochromatic, coherent, parallel beam having a diameter of a few millimeters.
ii. A sample cell carrying the dispersed particles (in liquid or air) at an appropriate concentration.
iii. A positive lens or set of lenses (Focusing lens).
iv. A detection system, located in the focal plane of the lens, to measure the intensity of the original or remaining light beam and the intensities of the scattered light by the particles at different angles
v. An interface and a computer to process the measured detector signals (scattering data).

For calculation of particle size distributions from scattering data, an appropriate optical model is required (Ma et al., 2000; Black et al., 1996; Keck and Muller, 2008). In general, either Fraunhofer approximation or Mie theory is used. Most of the commercial equipments use one of them for determination of particle size distribution by mathematical inversion process (Ma Zhenhua et al., 2000; Black et al., 1996; Keck and Muller 2008). Literature review shows that Mie theory provides a rigorous solution for the calculation of particle size distributions from light scattering data (Ma et al., 2000; Black et al., 1996; Keck and Muller, 2008). It is based on Maxwell's electromagnetic field equations and predicts scattering intensities for all particles, small or large, transparent or opaque. Table II.4 provides the assumptions used in Mie theory.

Table II.4: Summary - assumptions used in Mie theory for calculation of particle size distribution

- The particles being measured are spherical.
- The suspension is dilute, such at the scattered light is measured before it is re-scattered by other particles.
- The optical properties of the particles and the medium surrounding them are known.
- The particles are homogeneous.

Mie theory predicts the primary scattering response observed from the surface of the particle, with the intensity predicted by the refractive index difference between the particle and the dispersion medium. It predicts also how absorption of the particle affects the secondary scattering signal caused by light refraction within the particle. This information is particularly important for particles below 50 microns in diameter and is extremely important when the particle is transparent, as stated in the international standard for laser diffraction measurements (ISO 13320-1:1999).

The Fraunhofer approximation was used in early laser diffraction instruments, mainly because it is simpler to calculate and does not require input of the sample's optical properties. It is based on similar assumptions to Mie theory, but has some additional assumptions mentioned in table II.5.

Table II.5: Summary- additional assumptions used in Fraunhofer approximation for calculation of particle size distribution

- The particles being measured are opaque discs.
- Light is scattered only at narrow angles.
- The particles of all sizes scatter light with the same efficiency.
- The refractive index difference between the particle and surrounding medium is infinite.

These approximations hold at large particle sizes (above 50 microns in size) but are increasingly in error when measuring fine particles. The advancement in computer technology gave birth to sophisticated mathematical inversion algorithms which allow more complex optical models and which can better handle the ill-posed de-convolution problem (Ma et al., 2000). For example, Phillips–Twomey (1997) which solves the set of equations by smoothing the size distribution vector with an adjustable smoothing factor. Another known method is the chahine iterative scheme (Santer and Herman,1983). Boxman et al. (1991) also applied the Phillips–Twomey method, but they used it in conjunction with the fluctuations in time of the observed detector signals.

Disadvantages: Although, the laser diffraction technique has grown to maturity yet it still has some disadvantages in its application (Ma et al., 2000). A big disadvantage of the technique is its inability to measure the particle size of concentrated dispersions. This is because of the fact that all available de-convolution methods assume single scattering, that is, the light is scattered only once (Ma et al., 2000). This requirement restricts the particle concentration because high concentrations lead to multiple scattering, which in turn causes an overestimation of fines (Ma et al., 2000). Another disadvantage of the technique is that it is not adequately sensitive to detect the effects of few large particles if they are added or already present in a size distribution of finer particles (Ma et al., 2000). Similarly,

dependency of the size distribution on particle shape cannot be well explained by laser diffraction technique (Ma et al., 2000).

II.2.2 Acoustic attenuation spectroscopy

Literature review shows that acoustic attenuation spectroscopy, is a non-destructive and non-invasive technique that is quite matter of discussion in research and industrial circles in the last few decades because of its suitability for measuring particle size of colloidal particles (suspensions and emulsions) without need of dilution, on-line, under real process conditions, over a wide range of particle size (10nm to 1000 μm) and over a wide concentration range (0.5% vol. to 50% vol.) depending upon application (Dukhin et al., 2000, 2001a, 2001b; Challis et al., 2005; Alba et al.,1999). Challis et al. (2005) express that the principal reason for the considerable international scientific interest in the interactions of the ultrasound with particulate mixture is the need to measure the PSD without disturbing the mixture in a manner that will alter its state. According to Povey (2006) at a meeting of the Society of Chemical Industry in London, it was baldly stated that there was no other technique to match ultrasound in the characterization of nanoparticulate dispersions. Similarly McClements (2000) asserts ultrasonic spectroscopy has advantages over many existing particle-sizing technologies because it is non-destructive and non-invasive, is capable of rapid measurements and can be used to characterize systems which are concentrated and optically opaque. The technique has been employed in many studies for different applications. For example, Richter et al. (2006) employ it for characterization of polydisperse particles in micrometer range, Stolojanu and Prakash (2001) consider it for characterization of slurry systems, Tourbin and Frances (2009) monitor aggregation process of dense colloidal silica suspensions with this technique. Takeda and Goetz (1998) and other researchers like Hibberd et al. (1999) use the technique for characterization of flocculation in different applications. The applications of the technique in the domain of crystallization is described in the work of Hipp et al. (2000) , Mougin et al. (2003) and Li et al. (2004) etc. In general, the determination of particle size by means of acoustic attenuation spectroscopy is carried out in two steps: (i) measurement of acoustic attenuation spectrum (ii) interpretation of the acoustic attenuation spectrum in terms of particle size distribution (Dukhin et al., 2000, 2001a, 2001b; Challis et al., 2005; Alba et al., 1999).

II.2.2.1 Measurement of acoustic attenuation spectrum

When a sound wave of known frequency is passed through a particulate system, it interacts with the particles (transmission, reflection, absorption and scattering etc.) and as a result it undergoes attenuation (decrease in amplitude) that can be measured in terms of attenuation coefficient (Dukhin et al., 2000, 2001a, 2001b; Challis et al., 2005; Alba et al., 1999). It is defined as decrease in the amplitude of the sound wave per unit distance travelled and may be expressed as (McClements 2000):

$$\alpha = -\frac{1}{x}\ln\frac{A_x}{A_0} \qquad \ldots\ldots \quad (2.12)$$

Where A_0 is the initial amplitude of the sound wave (x=0) and A_x is the amplitude after it has travelled a distance x. The measured attenuation of the sound wave as a function of frequency is called acoustic attenuation spectrum. The six known loss mechanisms for the interaction of sound with a dispersed system are summarized in table II.6. However, only the four mechanisms (viscous, thermal, scattering, and intrinsic) make a significant contribution to the overall attenuation spectrum in most cases (Dukhin et al., 1996a, 1996b; Babick et al., 2000).

Table II.6: Summary: mechanisms of acoustic losses

Viscous losses: The viscous losses of the acoustic energy occur due to the shear wave generated by the particle oscillating in the acoustic pressure field. These shear waves appear because of the difference in the densities of the particles and the medium. This density contrast causes the particle motion with respect to the medium. As a result the liquid layers in the particle vicinity slide relative to each other. This sliding nonstationary motion of the liquid near the particle is referred to as shear wave (Dukhin et al., 1996a, 1996b).

Thermal losses: The reason for the thermal losses is the temperature gradients generated near the particle surface. These temperature gradients appear due to the thermodynamic coupling between pressure and temperature (Dukhin et al., 1996a, 1996b).

Scattering Losses: The mechanism of the scattering losses is quite different compared to those of the viscous and thermal losses. Acoustic scattering does not produce the dissipation of the acoustic energy. It is similar to the light scattering. Particles simply redirect the part of the acoustic energy flow. As a result the portion of the sound energy does not reach the sound transducer (Dukhin et al., 1996a, 1996b).

Intrinsic losses: The intrinsic losses of the acoustic energy occur due to the interaction of the sound wave with the materials of the particles and medium as homogeneous phases. (Dukhin et al., 1996a, 1996b).

Structural loses: The oscillation of the network of the interparticle links in the structured dispersed system causes structural losses. Thus, this mechanism is specific for the structured systems (Dukhin et al., 1996a, 1996b).

Electrokinetic loses: Oscillation of the charge particles in the acoustic field leads to the generation of the alternating electrical field and, consequently, alternating electric current. As a result a part of the acoustic energy transforms to electric energy and then irreversibly to heat (Dukhin et al., 1996a, 1996b). Structural losses and electrokinetic losses do not contribute significantly in overall attenuation in the system. Structural losses are prominent only in structured systems which require a quite different theoretical framework. Presently, there exists no theory for describing them as noticed by Dukhin et al. (Dukhin et al., 1996a, 1996b). The contribution of electrokinetic losses to the total sound attenuation is almost always negligible.

Acoustic attenuation spectrum is generally represented in term of a graph that is obtained as a result of passing a band of appropriate ultrasound waves through a dispersion and then plotting the resulting attenuation of each sound wave against respective frequency. Measurement of attenuations of sound waves of known frequencies is performed by the help of transducers that are generally built in acoustic attenuation equipment.

II.2.2.2 Interpretation of the acoustic attenuation spectrum in terms of particle size distribution (ECAH theory)

The second step in determination of particle sizing by this technique is interpretation of acoustic attenuation spectrum in terms of particle size distribution for which a suitable theory such as ECAH is

used. The word ECAH theory is based on names of four scientists Epstein, Carhart, Allegra and Hawley who contributed in development of this theory (Allegra and Hawley, 1972; Epstein and Carhart, 1953). ECAH theory is based upon fundamental laws of conservation of mass, energy, momentum, the thermodynamics equations of the state and stress-strain relations for isotropic elastic solids or viscous fluids and it is stated in terms of wave equations (Allegra and Hawley, 1972; Epstein and Carhart, 1953). ECAH theory describes how to calculate attenuation spectrum associated with a dispersion based upon its particle size distribution and knowledge of certain physical properties. Today, knowing the attenuation spectrum measured by help of transducers and information of certain physical properties of disperse and dispersion media provided by users, many commercially available acoustic equipments can extract the particle size distribution of disperse medium by mathematical inversion procedure using suitable software based upon appropriate algorithms (Dukhin et al., 2000, 2001a, 2001b; Challis et al., 2005; Alba et al. 1999).

The ECAH theory had been originally developed for the systems without particle-particle interaction (Dukhin et al., 2000, 2001a, 2001b; Challis et al., 2005; Alba et al., 1999). However, in many applications the theory provides correct interpretation of the experimental data even for volume fraction as large as 30%. ECAH theory (Allegra and Hawley, 1972; Epstein and Carhart, 1953) describes that the propagation of a sound wave through a heterogeneous media requires three potentials: compressional (Φc), thermal (ΦT) and viscous ($\Phi \eta$). Generally, ECAH theory does not result in a unique solution. Alba et al. (1999) showing the relationship between attenuation coefficient, frequency and particle size as in the figure II.5, asserts if attenuation is measured at a single frequency, it will correspond to four potential solutions of particle size. Two solutions will lie in the region of viscous attenuation, one in the Rayleigh scattering region, and one in the diffraction zone. However, if two frequencies are used, then each of them will produce four solutions of particle size. That is why in a practical measurement, a band of frequencies is used instead of a single frequency. This helps in finding a single solution by comparing the solutions corresponding to each frequency.

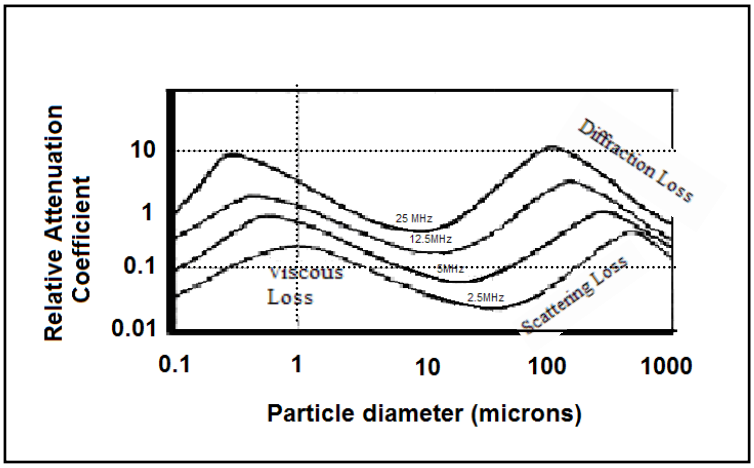


Fig. II.5: Relationship between attenuation coefficient, frequency and particle size.

Disadvantages: There are certain disadvantages of the acoustic attenuation spectroscopy. For example, the technique requires knowledge of numerous physical properties of the dispersed and dispersion medium that sometimes are difficult to acquire. This makes application of the technique difficult (Babick et al., 2000). Another disadvantage of the technique is that it is not capable of measuring the particle size of the dispersions at very low concentration (normally but not essentially < 1 wt. %). Similarly, the presence of foam and bubbles in the sample may disturb the acoustic signals misleading to false results (Challis et al., 2005). Multiple scattering is another problem that has been reported in acoustic measurement in suspensions of silica in the particle size range of few nanometers (Tourbin and Frances, 2009).

II.2.3 Dynamic light scattering

Dynamic light scattering (DLS) is also known as photon correlation spectroscopy or Quasi-elastic light scattering. Literature review (Tscharnuter, 2000; Xu, 2000; Dalgleish and Hallett, 1995) indicates that discovery of the technique roots to beginning of twenty century when it was discovered that there exists a relationship between temporal fluctuations in the average scattered light intensity and motion of the particles (diffusion coefficients). Einstein (1910) aready had published a relationship between diffusion and size. So, in principal, two works provided foundations for particle sizing with the help of DLS (Tscharnuter, 2000). The advent of the laser, development of digital correlators and appropriate algorithms resulted in development of commercial DLS instruments (Tscharnuter, 2000). The relationship of Brownian motion with (i) particle size and (ii) rate of fluctuation of intensity of scattered light, form the foundation of particle sizing by DLS (Tscharnuter, 2000; Xu, 2000; Dalgleish and Hallett, 1995).

II.2.3.1 Brownian motion and particle size

Particles in a suspension experience Brownian motion (movement of the particles due to random collisions with the molecules of the liquid that surrounds the particles). The speed of Brownian movement that is defined by translational diffusion coefficient (*D*) depends upon size of the particle. The larger the particle, the slower the Brownian motion will be and vice versa. Stokes-Einstein equation (Einstein, 1910) defines the relationship between translational diffusion coefficient and size of the particle as:

$$d(H) = \frac{kT}{3\pi\eta D} \qquad \ldots\ldots (2.13)$$

Where, *d (H), D, k, T* and η represent hydrodynamic diameter, translational diffusion coefficient, Boltzmann's constant, absolute temperature and viscosity respectively. Hydrodynamic diameter *d (H)* refers to how a particle diffuses within a fluid. It is the diameter of a sphere that has the same translational diffusion coefficient as the particle. It directly depends upon temperature, viscosity and

translational diffusion coefficient. The literature review (Tscharnuter, 2000; Xu, 2000; Dalgleish and Hallett, 1995; Malvern Instruments Technical Notes MRK656-01) shows that the translational diffusion coefficient depends not only on the size of the particle core, but also on any surface structure, as well as the concentration and type of ions in the medium.

Ionic strength of medium: The ions in the medium and the total ionic concentration can affect the particle diffusion speed by changing the thickness of the electric double layer generally called the Debye length (*1/K*). Thus an extended double layer of ions around the particle is created by a low conductivity medium. This results in a decrease of the diffusion speed and finally the development of a larger hydrodynamic diameter. Conversely, higher conductivity media can suppress the electrical double layer and the hydrodynamic diameter.

Surface structure: Changes to the surface of a particle that affect the diffusion speed can modify the hydrodynamic diameter of the particle. For example, the way by which polymer particles interact may lead to surface changes, resulting in a decrease in diffusion speed and ultimately a change in particle size. Similarly, the nature of the surface and that of the polymer can affect the polymer conformation resulting in a change of the hydrodynamic diameter of the particle.

Non-spherical particles: The change in shape of a particle may affect the diffusion speed and ultimately hydrodynamic size of the particle. For example a small change in the length of rod-shaped particles affects diffusion speed and thus results in change of hydrodynamic size of the particle whereas changes in the diameter of rod-shaped particles do not change diffusion speed and ultimately no change in hydrodynamic size of particle is observed by DLS.

II.2.3.2 Brownian motion and rate of intensity fluctuation of scattered light

If a cell, containing stationary particles, is illuminated by a laser and a frosted glass screen is used to view the sample cell, a speckle pattern can be seen as illustrated in figure II.6 (Malvern Instruments, Technical note MRK656).

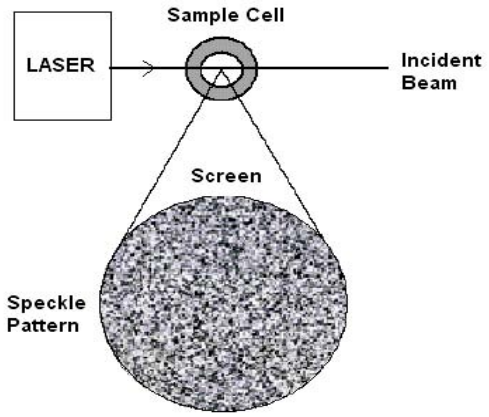


Fig. II.6: Speckle pattern in dynamic light scattering.

The bright spots of light in the speckle pattern are formed where scattered light of the same phase interfere constructively. Dark spots are observed where the phase additions of the scattered light are mutually destructive and cancel each other. In a real system in which particles undergo Brownian motion, a dynamic speckle pattern is observed because the phase addition from the moving particles constantly evolves and forms new patterns. The rate at which these intensity fluctuations occur depends on the size of the particles. Figure II.7 shows how intensity fluctuations are function of particle size (Malvern Instruments, Technical note MRK65642).

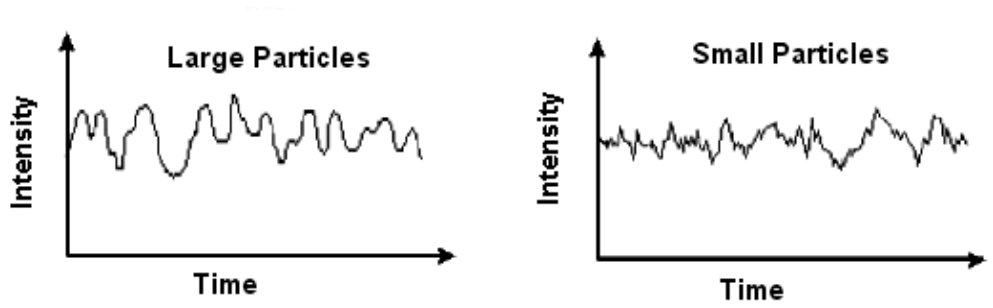


Fig. II.7: Intensity fluctuations in two samples of different particle sizes.

Determination of particle size in a DLS instrument: The figure II.8 shows a schematic of a dynamic Light scattering (DLS) instrument for particle size (Tscharnuter, 2000; Xu, 2000; Dalgleish and Hallett, 1995; Malvern Instruments Technical Notes MRK656-01). A laser is generated through source to illuminate the sample in measurement cell. Attenuator is used to reduce or increase the intensity of the laser according to nature of the samples and application. A detector is used to measure the scattered light whereas a correlator is a signal comparator. It is designed to measure the degree of similarity between two signals, or one signal with itself at very short time intervals (order of a millisecond or tens of milliseconds).

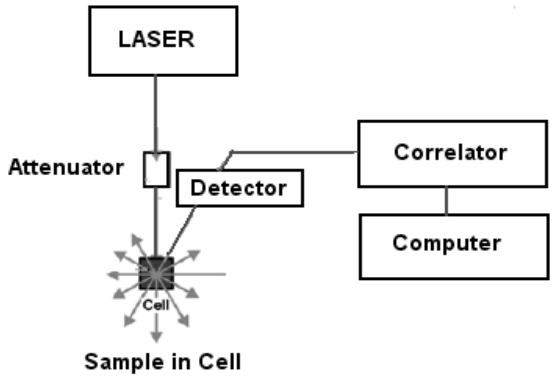


Fig. II.8: Schematic of a dynamic light scattering (DLS).

A correlator constructs a function called the intensity correlation (Tscharnuter, 2000; Xu, 2000; Dalgleish and Hallett, 1995, Malvern Instruments Technical Notes MRK656-01):

$G(\tau) = \langle I(t).I(t+\tau) \rangle$ ……(2.14)

Where τ = the time difference (the sample time) of the correlator.

For a large number of monodisperse particles in Brownian motion, the correlation function (given the symbol [G]) is an exponential decaying function of the correlator time delay τ:

$G(\tau) = A [1 + B \exp(-2\Gamma\tau)]$ ……(2.15)

Where A is the baseline of the correlation function and B, the intercept of the correlation function.

$\Gamma = Dq^2$ …… (2.16)

Where D represents the translational diffusion coefficient.

$q = (4 \pi n / \lambda_o) \sin (\theta/2)$ …….(2.17)

Where, n is the refractive index of dispersant, λ_o the wavelength of the laser and θ the scattering angle.

For polydisperse samples, the equation can be given as:

$G(\tau) = A[1 + B\, g1(\tau)^2]$ …… (2.18)

Where $g_1(\tau)$ is the sum of all the exponential decays contained in the correlation function. Size may be obtained from the correlation function using different algorithms.

Literature review explains that two approaches are mostly adopted. First Cumulants analysis as defined in ISO13321: 1996. This approach fits a single exponential to the correlation function for obtaining the mean size (z-average diameter) and estimate the width of the distribution (polydispersity index).

Second approach such as Non-negative least squares (NNLS) or CONTIN consider fitting of a multiple exponential to the correlation function to obtain the distribution of particle sizes (Malvern Instruments Technical Notes MRK656-01).

II.2.4 Summing up - comparison of particle sizing techniques

The particle sizing equipments made by different commercial manufacturers may differ in some features. Considering particle sizing equipments of Malvern Instruments, the table II.7 provides a comparison of the techniques.

Table II.7: Comparison of particle sizing techniques

	Laser diffraction technique	Acoustic attenuation spectroscopy	Dynamic light scattering
Particle size range:	For suspensions: 20 nm to 2000 µm (Reliability is poor below 200 nm approximately)	For suspensions: 1 nm to 1000 µm	For suspensions: 0.6nm to 6µm
	For powders: 200 nm to 2 µm	For powders: Not feasible	For powders: Not feasible
Concentration of the sample:	Approximately below 1 %wt.	1 to 50 %wt.	Approximately below 1 %wt.
Quantity of the sample required:	About 1 g	About 500 g	About 1 g
Equivalent diameter:	Volume based diameter	Volume based diameter	Hydrodynamic diameter
Principles:	Fraunhofer theory Mie theory	ECAH theory	Brownian movement Intensity correlating technique
Time of a single measurement:	1 minute approximately	2-10 minutes	2-3 minutes
Knowledge of physical properties required:	Refractive index of media	Density Sound velocity Thermal dilation Thermal conductivity Heat Capacity Viscosity Shear rigidity	Refractive Index of media Absorption Viscosity Temperature
Real time:	No	Yes	No
Online application:	Possible	Possible	Possible

II.3 Colloid preparation by wet grinding processes

II.3.1 General considerations

Grinding, size reduction or comminution is carried out to increase surface area of a material, to prepare a specific particle size distribution of a material or/and to separate one material from others etc. (Siegfried and Klaus, 2005). Size reduction process leads to advantages such as enhancement in reactivity, solubility, purity, strength, taste, color-intensity and miscibility of materials (Siegfried and Klaus, 2005).

Based on literature review, the important factors that considerably influence a grinding process may be divided into four classes as mentioned in table II.8:

Table II.8: Important factors influencing a grinding process
I. Operating parameters of the mill: For example, dispersing time, throughput, stirred tip speed, grinding media size, grinding media material (density, elasticity and hardness), and filling ratio of the grinding media etc. **II. Operating mode of the mill:** e.g., one, multiple passage mode, pendulum or circuit operation. **III. Formulation:** Such as solid concentration of the particles, fluid (water, solvents and resins etc.) and proportion of additive or dispersing agents etc. **IV. Mill geometry:** Such as type of the mill, size and dimension of the mill etc.

Table II.9 lists the names of important wet grinding mills and explains when wet grinding is preferred to dry grinding.

Table II.9: Wet grinding: different mills and reasons to prefer wet grinding
Important wet grinding mills: • Grinding media mills (Tumbling and vibrating mills etc.) • Szego mill, • Roller & ring-roller mills • Stirred (agitated) media mills **Wet grinding is preferred to dry grinding when:** • The feed already exists in form of suspension or/and • The product is desirable in form of suspension • The material is explosive or toxic and hazards may be avoided in a better way in form of suspension • It is difficult to control agglomeration of feed in powder form as compared to the liquid form (suspension)

Literature review brings out that tumbling ball mills that were mostly used in the past for wet fine and ultra grinding had limited power density due to limited number of revolutions at which the grinding media are centrifuged at the chamber wall (Kwade, 1999). This turns the attention of the scientists, researchers etc. to stirred media which, as compared to tumbling and vibrating mills, are more suitable for producing high number of stress events per unit time and unit volume creating an appropriate stress intensity resulting in lower consumption of specific energy (Kwade, 1999).

II.3.2 Designs of stirred media mills

In the last two decades, many designs of stirred media mills have been developed in the industry for specific needs. Bernotat and Schonert (2005), explain that in general, a stirred media mill consists of horizontal or vertical cylindrical housing carrying an agitator shaft equipped with perforated rings, disks or pins. The agitator shaft is capable of running along the axis of the mill. Beads or balls of glass, steel or ceramic etc. are filled in the cylindrical housing to serve as grinding medium. The feed (suspension) is forced into the mill with help of a pump. A screen or slot hold back the grinding media at the product discharge. Figure II.9 shows a simple schematic of a stirred media mill (Bernotat and Schonert, 2005).

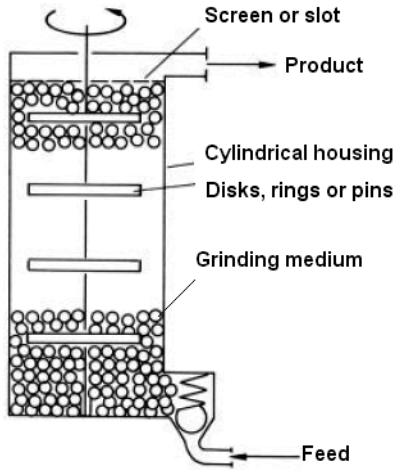


Fig. II.9: Important parts of stirred media mill.

Three types of stirred media mills can be distinguished on basis of design of chamber and stirrer, as mentioned by Kwade (1999) in the figure II.10.

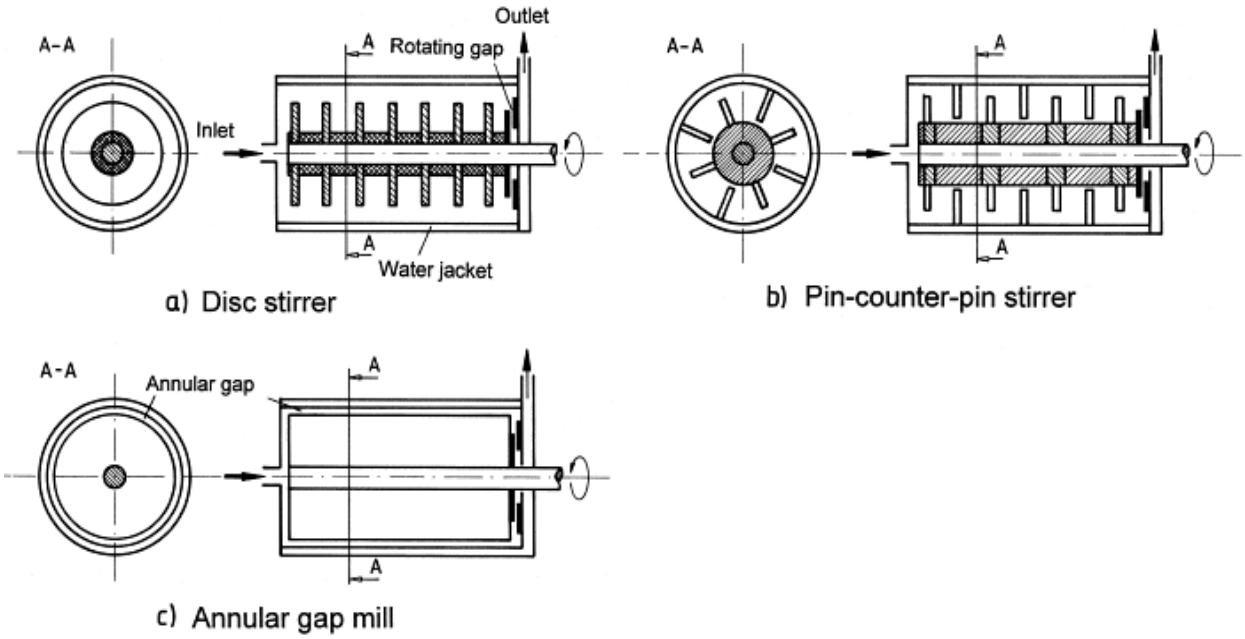


Fig. II.10: Three designs of stirred media mills pointed out by Kwade

Kwade (1999) explains that a stirred media mill with disc stirrer is considered as the simplest design in which energy is transferred from the stirrer to the grinding media and product mainly by adhesion. Sometimes there are holes, slots and slits etc. on the disks in order to provide additional energy by means of displacement forces. In pin-counter-pin stirrer design, grinding media and product move by displacement forces. At an identical circumferential speed, the mills with pin-counter-pin stirrer design show larger power density as compared to disk mills. The highest power density can be obtained in a grinding chamber of an annular gap mill (Kwade 1996).

II.3.3 Issues and approaches in stirred media milling

In the recent past, many studies have been carried out to understand various aspects of stirred media milling. The studies differ in terms of grinding material, stabilization mechanism, design of mill, and emphasis of investigation etc. For example, Belfadhel et al. (1999) in a study focus on grinding of dispersions of TiO_2 in stirred media mill (Drais Perl mill) both in batch and continuous grinding. Optimal conditions in batch mode have been reported by them based on grinding rate and specific energy consumptions. Their work combines grinding kinetics of the dispersion with resident time distribution function in order to predict the size distribution of continuous ground product in the mill. The important conclusions from their work is that the increase in residence time, obtained with low feed flows and using small beads favor in obtaining smaller particles in the wet grinding process. In another study Belfadhel and Frances (2001) investigate the wet grinding of hydrous alumina in Drais perl mill (stirred media mill) in presence of sodium metaphosphate (an additive). They discuss, in particular, the relationship between density of slurry and specific energy, effects of initial size of product, stirrer speed and size of beads.

Garcia and Frances have investigated various aspects of grinding of aqueous dispersions of $CaCO_3$. In a study on wet grinding of dense aqueous suspensions of $CaCO_3$, in a stirred media mill (Drais perl mill), Garcia et al. (2003), investigate the rheological behavior and granulometric properties. They characterize and compare the grinding of aqueous suspensions of $CaCO_3$ with and without addition of dispersing additive sodium polyacrylate. In absence of an additive, they explain that aggregation process starts to influence the grinding after few minutes of milling.

In another paper, Garcia et al. (2001) report changes of surface and volume properties of calcite during a batch wet grinding process. They indicate that an agglomeration phenomenon takes place under shear, due to the increase of the amount of fines produced during the process. They propose a kinetic model by considering the sub-populations of fragments and agglomerates. The size distribution of ground particles have been fitted by a linear combination of log-normal laws. Similarly, in another interesting study, Kwade (2003, 2007) proposes a stressing model that helps in describing various aspects of grinding behavior in stirred media mill. The model takes into consideration two approaches to explain grinding behavior: mill related approach and particle related approach. Kwade (2003) expresses that a grinding process may be examined from above stated perspectives for optimization.

In recent past, the work of Stinger et al. (2005) focuses on production of stabilized nano dispersions. They emphasize the control of particle-particle interaction that plays a crucial role when particle enter into range of nano particle during wet grinding. An interesting finding in their work is that better grinding results can be achieved at the same specific energy input when higher solid mass fractions are used. They assert that the problem in this approach is that higher concentrations lead to higher viscosities that may block the feed flow in the grinder, circulating pipes and the pump.

In another study, Peukert (2004), attempts to differentiate the influence of material properties and mill properties in the production of fine particles. He asserts that the lack of knowledge of influence of material properties is reflected in the disappointing experience that each grinding test with a new dispersion has to start from scratch. In this regard, we can refer to the work of Frances (2004) on modeling of fine wet grinding processes in bead mills by population balance. The aim of a grinding model is to predict the product quality as a function of the initial material properties and the operational conditions. Considering batch and continuous grinding processes, the mentioned paper discusses the population balance solutions.

In the literature, some studies focus on the online particle sizing during stirred media milling. Wang and Forssberg (2006), for example, compare the grinding results for silica and carbonate dispersions using two types of stirred media mills (i.e. DCP superflow 12 and PML H/V). They use scanning mobility particle sizer (SMPS) and an acoustic particle sizer (ASP-100) for determining the particle size of the suspension. The disadvantage of the particle sizing by scanning mobility particle sizer (SMPS) is that it requires the sample to be converted into aerosol by impact of high velocity air flow. In another study, Bordes et al. (2002) report experimental results on the online characterization of particle size by means of an optical analyzer (Turbiscan) in a batch grinding process carried out in a stirred media mill (Drais Perl mill). The influence of various operating parameters (solid volume fraction, stirring rate and feed flow rate) on stability of the system has been discussed in their work. Though, many approximations have been made in their work in characterization, yet still there study reports a good agreement with results obtained through electron microscopic and size analysis in dilute conditions.

II.3.4 Stress number and stress intensity

The various aspects of comminution process in stirred media mill have been explained by Kwade et al. (1999a, 1999b, 2003, 2007) on the basis of number of stress events (sometimes referred as stress number) and stress intensity. Later on this approach was used in many other studies too. Number of stress events refers how often each feed particle (and the fragments arising from the feed particle) is stressed per unit time in the grinding mill whereas stress intensity refers to intensity of the stress as obvious from the verbal meaning of the term.

Kwade (2003) asserts that number of stress events and corresponding stress intensities determine the comminution result. Since the stress intensity can be considered to be the specific energy consumed at each stress event, the overall specific energy consumption of the mill is a good measure for the product of stress number and stress intensity (Kwade 1999a, 1999b, 2003, 2007). Therefore, at constant stress intensity the product fineness can be correlated either with the stress number or the specific energy input.

Number of stress events (*SN*)

In a batch grinding process, the average number of stress events (SN) (sometimes referred as stress number) is given by (Kwade 1999a, 1999b, 2003, 2007, Becker at al. 2001):

$$SN = \frac{N_C P_S}{N_P} \qquad \ldots\ldots (2.19)$$

Where N_c denotes the number of media contacts, P_s the probability that a particle is caught and sufficiently stressed at a media contact and N_p the number of product particles inside the mill.

Kwade assumes that the number of media contacts (N_c) is proportional to the number of revolutions of the stirrer and to the number of grinding media (N_{GM}) in the chamber as shown in the following expressions:

$$N_C \propto n \cdot t \cdot N_{GM} \propto nt \frac{V_{GC} \varphi_{GM} (1-\varepsilon)}{\frac{\pi}{6} d_{GM}^3} \qquad \ldots\ldots (2.20)$$

Where, n and t denote number of revolutions of the stirrer per unit time and comminution time respectively whereas V_{GC} is the volume of grinding chamber, φ_{GM} is the filling ratio of grinding media (dimensionless), ε is porosity of the bulk grinding media, and d_{GM} is the diameter of the grinding media. According to Stadler et al. (1990) and Bunge (1992) in case of desagglomeration and cell disintegration, probability (*Ps*) is proportional to the surface of the grinding media. i.e.

$$P_s \propto d_{GM}^2 \qquad \ldots\ldots (2.21)$$

In case of grinding of crystalline materials, *(Ps*) is proportional to the active volume between two grinding media that is proportional to diameter of the grinding media (Kwade 1999a, 1999b, 2003, 2007; Becker at al., 2001):

$$P_s \propto d_{GM} \qquad \ldots\ldots (2.22)$$

The number of product particles (*Np)* is proportional to the overall volume of the product particles that can be given as (Kwade 1999a, 1999b, 2003, 2007, Becker at al. 2001):

$$N_P \alpha V_{P,ges} = V_{GC} (1 - \varphi_{GM} (1 - \varepsilon)) c_v \qquad \ldots\ldots (2.23)$$

Where, c_v is the volume solids concentration of the product suspension. From the above equations, the following expressions can be derived:

Case of desagglomeration /disintegration:

$$SN \propto \frac{\varphi_{GM}\left(1-\varepsilon\right)}{\left\{1-\varphi_{GM}\left(1-\varepsilon\right)\right\}c_V}\frac{n\cdot t}{d_{GM}} \qquad \ldots\ldots (2.24)$$

Case of grinding of crystalline materials:

$$SN \propto \frac{\varphi_{GM}\left(1-\varepsilon\right)}{\left\{1-\varphi_{GM}\left(1-\varepsilon\right)\right\}c_V}\frac{n\cdot t}{d_{GM}^{2}} \qquad \ldots\ldots (2.25)$$

Stress intensity (*SI*)

In case of grinding crystalline materials, with increasing stress intensity a finer product is achieved for a certain number of stress events. Against that in case of desagglomeration and disintegration at a constant stress number the stress intensity has nearly no effect as long as the stress intensity is high enough to break the agglomerates or cells (Kwade 1999a, 1999b, 2003, 2007, Becker at al. 2001).

Based on the work of Bunge (1992), Reinsch et al. (1997), Winkler et al. (1987) and on the following assumptions, Kwade (1999a, 2007) derives a characteristic parameter for expressing stress intensity (equation 2.26):

- Only single particles are stressed intensively between the grinding media and, therefore, the stressed particle volume does not depend on the grinding media size.
- The tangential velocity of the grinding media is proportional to the circumferential speed of the discs.
- The diameter of the discs is kept constant.
- The elasticity of the feed material is much smaller than that of the grinding media.

$$SI \propto SI_{GM} = d_{GM}^{3}\rho_{GM}v_t^{2} \qquad \ldots\ldots (2.26)$$

Kwade (1999a, 2007) further asserts if elasticity of the feed material is about the same or higher than that of the grinding media material (e.g., comminution of ceramic materials) the modulus of elasticity of the product (El_p) , and of the media material (El_{GM}) must be taken into account. The deformation of the grinding media can be expresses as, according to Becker et al. (1997).

$$SI \propto SI_p = d_{GM}^{3}\rho_{GM}\upsilon_t^{2}\left(1+\frac{El_p}{El_{GM}}\right)^{-1} \qquad \ldots\ldots (2.27)$$

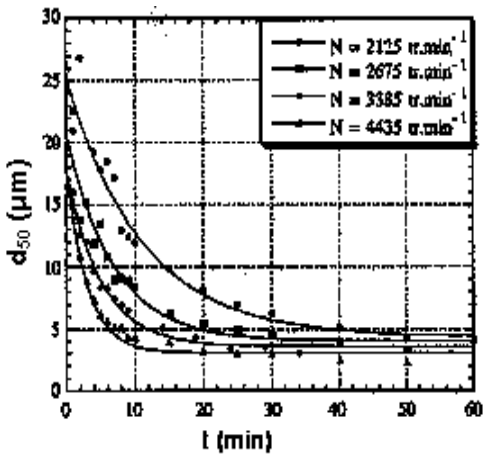
According to Kwade (1999a, 2007) the two parameters of SI_{GM} and SI_P may be considered for measuring the stress intensities in stirred media mill. However, the real intensities can only be described by a distribution.

II.3.5 Important operating parameters

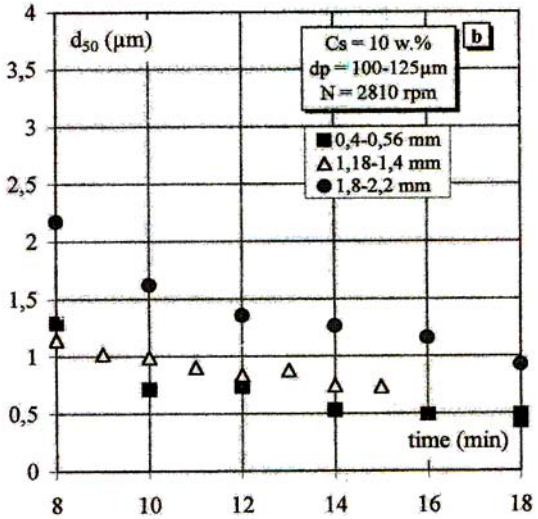
There are several operational parameters that may affect the size reduction process in stirred media mills such as size, nature and filling ratio of grinding medium, speed of rotation of the stirrer, initial feed size of particles, density and concentration of the dispersions. The effects of a parameter on size reduction process are studies, in general, keeping other operating conditions constant. Therefore, description of these effects is relative. In older publications, the product fineness often has been presented as a function of the comminution time. However following the approach of Kwade, many researchers use the stress energy and sometimes stress number to describe product fineness.

Speed of agitator: It is an important parameter in size reduction because it affects the number and intensity of collisions between the grinding media and particles. In general, the rise in speed of grinding media results in quicker fragmentation of particles. Varinot et al. (1999) shows the effects of speed of agitator on particle size of carbon powder as in figure II.11. Similar tendency was observed by Belfadhel and Frances in stirred media milling in case of alumina hydrate (Belfadhel and Frances, 2001) and in case of titanium dioxide (Belfadhel and Frances, 1999).

Size of grin ding media: Specific energy can be reduced considerably by selecting the appropriate diameter of grinding media as a function of size of final product. Belfadhel and Frances (2001) illustrate the effects of three diameters of grinding media on the size reduction of alumina hydrate in a stirred media mill as shown in figure II.12. In nano-milling, the production of nano particles, in general, is favoured by use of fine grinding media. The selection of smaller size of grinding media is limited to a certain extent. After a certain size, the problem of separation of grinding media from suspension becomes significant.



(Fig. II.11)



(Fig. II.12)

Fig. II.11: Effects of speed of agitator on particle size
Fig. II.12: Effects of size of grinding media

Filling ratio of grinding media: Engels (1965) and Bosse (1958) stated that the filling ratio of the grinding media had a great influence on grinding results. With increasing filling ratio of the grinding media the number of media contacts increases and the distance between the individual grinding media decreases. According to Bosse and Engels particularly the decrease in distance between media causes an improvement of the grinding result. But above a certain filling ratio of grinding media the grinding result brings negative effects because too small distance between grinding media limit the freedom of motion. For each design (size and type) of mill, there exists an optimum filling ratio (Kwade 1996). The figure II.13 shows effects of filling ratio as studied by Kwade (1996).

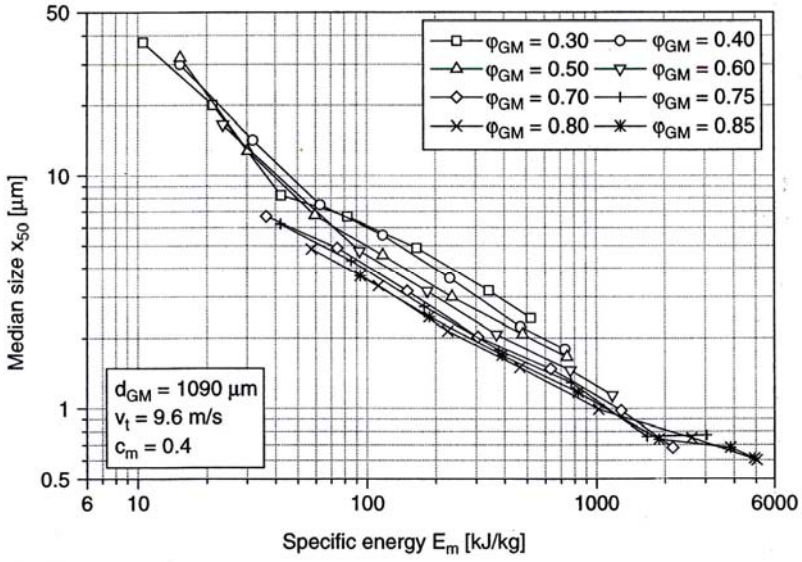


Fig. II.13: Effects of filling ratio of grinding media

Figure II.14 shows another example of effects of filling ratio of grinding media from work of Mingzhao et al. (2006) for grinding of Calcite.

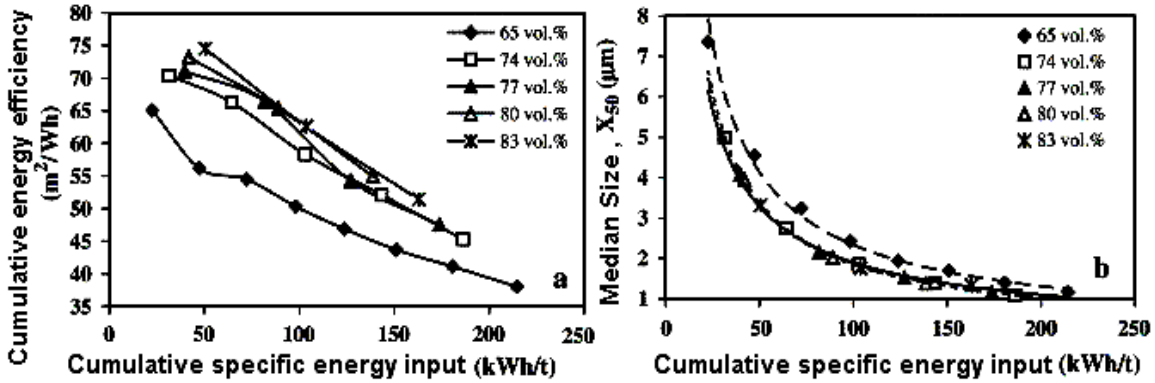


Fig. II.14: Effects of filling ratio of grinding media

Concentration: The concentration of dispersions in stirred media mills determines, among others, how many particles are located in a certain volume. In case of stressing of a single particle, the number of stress events per particle and time decreases with increasing solid concentration and with increasing number of fee and/or product particles. Kwade (2007) studied the effects of mass concentration by varying it from 0.1 to 0.5 without addition of dispersing agent or additive. The figure II.15 shows the results. It may be observed that at lower values of specific energy such as 100 KJ/Kg, the change in concentrations of the dispersion make almost no effect on the particle size. At moderately high values of specific energy such as 1000 KJ/Kg, it may be observed that increase in concentration of the dispersions favors in achievement of particles of smaller sizes. It must be noticed that at 1000 KJ/Kg the respective median particles sizes of the dispersions are close to 1μm (i.e. relatively coarse particles). However, at high values of specific energy, that are required in production of ultra fine and nanoparticles, the effects of concentrations of the dispersion are less clear.

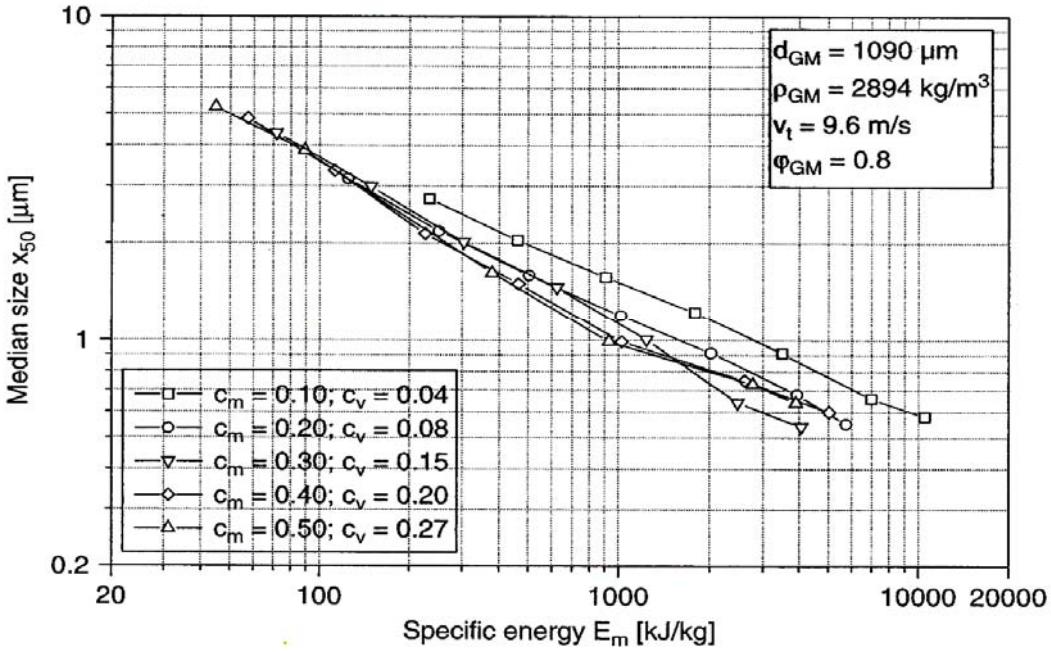


Fig. II.15: Effects of concentration of particles on median size

Analyzing the batch grinding of black carbon in a stirred media mill, Varinot et al. (1999) reported that a solid concentration between 5 and 20% is favourable in achievement of smaller particles. On the contrary, the work of Belfadhel and Frances (2001) on wet grinding of alumina hydrate brings that higher fineness can be achieved in the dispersions by using dispersion of lower concentrations. The reason for such differences is based upon the fact that the increase in solid concentration affects the state of particles in two manners. On one side, the probability that particles are captured and stressed between two grinding beads is increased. This results in better size reduction. On the other side, the increase in concentration of the dispersion, increases the viscosity of the dispersion that may lead to

agglomeration and unsmooth flow of the dispersion etc. Another main problem in understanding the effects of concentration on size reduction process is the lack of suitable particle sizing techniques that could work without diluting the sample. The recent advent of acoustic attenuation spectroscopy which is known for particle sizing on line, under the real process conditions and without diluting the sample, may be an interesting option to analyze the effects of solid concentration on the grinding results.

Pour conclure

Les procédés de broyage en voie humide reposant sur la technologie des broyeurs à billes agités permettent l'obtention de particules fines ou de nanoparticules en suspension concentrée. Il est essentiel d'assurer la stabilité des fragments de particules produits au cours de l'opération. Nous avons rappelé dans ce chapitre les principales forces attractives et répulsives s'exerçant au sein des milieux colloïdaux. Des additifs, provoquant une répulsion électrostatique ou stérique, voire électrostérique sont couramment utilisés dans les procédés de broyage en voie humide pour stabiliser les suspensions produites. La stabilité électrostatique induite par une modification des propriétés physico-chimiques (pH, force ionique, …) constitue une deuxième voie possible dans certaines applications pour améliorer la stabilité des suspensions broyées.

Concernant la caractérisation de la taille des particules en suspension, les technologies les plus usuelles reposent sur des méthodes optiques. Parmi celles-ci, nous considérerons plus particulièrement dans ce travail la diffraction laser et la diffusion dynamique de la lumière. La diffraction laser est une technique très répandue, elle permet la caractérisation de la taille de particules entre 20 nm et plusieurs millimètres. La méthode nécessite toutefois une très faible concentration en particules dans l'échantillon analysé, ce qui exige de fait une pre-étape de dilution importante lorsqu'on considère des dispersions traitées par broyage en voie humide. La diffusion dynamique de la lumière, reposant sur l'interprétation de l'intensité diffusée par des particules animées par mouvement Brownien permet la mesure de taille de particules entre 0,6 nm et quelques microns ; elle nécessite également de travailler en milieu relativement dilué. La spectroscopie acoustique qui est basée sur la mesure de l'atténuation d'ondes sonores au travers du milieu dispersé, permet quant à elle une mesure des propriétés des particules de taille comprise entre quelques dizaines de nm et 1000 µm. Du fait qu'elle ne nécessite pas une dilution des échantillons, elle semble une alternative intéressante par rapport aux méthodes optiques, d'autant plus qu'elle peut s'effectuer en ligne du procédé. Elle possède toutefois quelques désavantages, en particulier le fait qu'il est nécessaire de connaître un nombre conséquent de propriétés physiques des phases dispersée et continue pour pouvoir interpréter correctement le spectre d'atténuation acoustique et déduire la distribution de taille des particules en suspension. Le problème de diffusion multiple qui a été rapportée par certains auteurs constitue un autre inconvénient lors du traitement de l'information acoustique. Enfin, comme nous l'avions indiqué en introduction, il existe un manque de connaissances sur l'utilisation de la spectroscopie acoustique dans des milieux dispersés contenant plusieurs constituants.

Dans la dernière partie de ce chapitre, nous avons présenté quelques généralités sur les procédés de broyage en voie humide, reposant sur l'utilisation des broyeurs à billes agités.

Nous avons précisé en particulier l'approche couramment utilisée pour quantifier l'efficacité

énergétique de ce procédé et nous avons présenté quelques résultats de la littérature illustrant l'influence des paramètres opératoires sur le résultat de l'opération. La distribution de taille du produit qui est très fortement modifiée au cours de l'opération constitue une donnée essentielle pour caractériser la qualité du produit broyé.

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Research Methodology and Preliminary Work

* *As per requirements of the university, a preface in the beginning and concluding remarks at the end of the chapter have been given in French.*

Préface en français

Après avoir précisé les objectifs et le contexte scientifique du sujet, nous présentons dans ce chapitre les caractéristiques des matériaux utilisés ainsi que les différentes techniques analytiques et les équipements avec lesquels nous avons menés les différents essais expérimentaux.

Le carbonate de calcium constitue le matériau support de cette étude. Des solutions aqueuses de différentes concentrations seront utilisées. Selon les objectifs poursuivis, qui font l'objet des chapitres suivants, des additifs comme le polyacrylate de sodium ou des impuretés solubles (telle que le nitrate de sodium) ou quasiment insolubles (comme le carbonate de magnésium) seront utilisées.

Comme nous l'avons déjà mentionné, nous utiliserons différentes techniques de caractérisation (diffraction laser, spectroscopie acoustique, diffusion dynamique de la lumière). Les principes physiques des méthodes employées ont été présentés au chapitre II. Dans ce chapitre, nous rapportons les données techniques des appareils utilisés (Malvern Mastersizer 2000, Zetasizer nano ZS, Ultrasizer). De même, nous détaillons ici les différents éléments constitutifs du broyeur à billes agité de laboratoire (Broyeur Lab Star de Netzsch) avec lequel nous avons réalisé les essais de broyage.

Contrairement aux techniques optiques utilisées, la spectroscopie acoustique est plus délicate à mettre en œuvre. Des essais préliminaires de mesure du spectre d'atténuation acoustique dans des suspensions aqueuses de carbonate de calcium sont présentés en fin de chapitre.

III. Research Methodology and Preliminary Work

III.1 Materials

The calcium carbonate was the principal material used in this study. The suspensions of calcium carbonate were prepared in water. In different phases of the study, different impurities and/or additives were added in the suspension depending upon objectives and conditions of the experiments. The details are given in respective chapters. There are many reasons for selection of the aqueous suspensions of $CaCO_3$, in the study, such as reasonable price, good shelf life, adequate storage conditions, easy procurement, inertness for the equipments used, low hazards and risks in handling, easiness in disposal after experiments, applications of the results in many industries and above all, availability of satisfactory literature on $CaCO_3$. Calcium Carbonate of two different particle sizes (fine and coarse) was used in the study. We distinguish them by Calcium Carbonate (A) and Calcium Carbonate (B) in this manuscript.

III.1.1 Calcium carbonate (A)

Manufacturer:	Merck KGaA Germany
Preparation method:	Precipitation
Purity:	> 98%,
Density:	2.93 g/cm^3 at 20˚C
Bulk density:	~ 400-700 kg/m^3
Solubility in water at 20˚C:	0.014 g/l
Thermal decomposition:	> 825˚C
Mean particle size:	1.6 µm

A Mastersizer 2000 of Malvern Instruments Limited, U.K., which is based on laser diffraction technique, was used to find the mean particle size of $CaCO_3$ (in powder form). It was found to be 1.6µm.

III.1.2 Calcium carbonate (B)

Manufacturer:	Merck KGaA Germany.
Purity:	> 99%,
Density:	2.656 g/cm^3 at 20˚C
Thermal decomposition:	> 825˚C
Specific surface area (BET):	0.5 m^2/g
Hardness in the Mohs scale:	3
Mean particle size:	30 µm in powder form, using laser diffraction technique (Malvern Mastersizer 2000)

Its particle size distribution, as shown in figure III.1, explains that most of the particles had a size between a few microns and one hundred microns. To study the shape of $CaCO_3$, scanning electron microscopy (SEM) was employed. It was observed that the product is constituted by compact aggregates made of rhombohedral particles of about 30µm in size, as shown in figure III.1. A reasonable agreement was found in the results of both techniques.

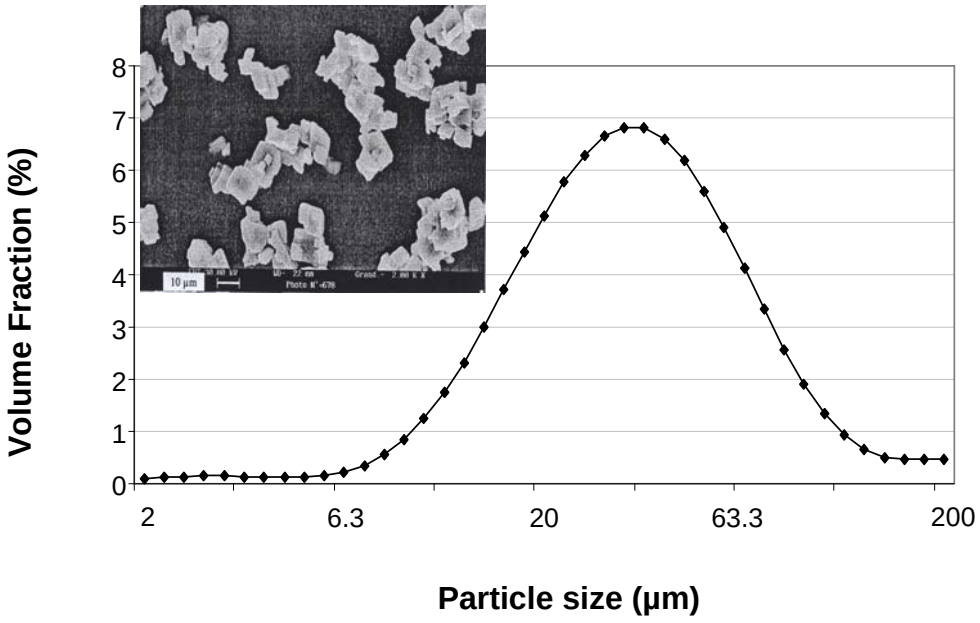

Fig. III.1: Particle size distribution and shape of $CaCO_3$

III.1.3 Magnesium carbonate

Type:	Magnesium carbonate (anhydrous)
Manufacturer:	Fisher Scientific, U.K.

Solubility in water at 20˚C:	Insoluble
Density:	2.958 g/cm^3 at 25˚C
Mean particle size:	7.3 μm in dry form, using laser diffraction technique (Malvern Mastersizer 2000)

III.1.4 Sodium nitrate

Manufacturer:	Fisher Scientific, U.K.
Density:	2.26 g/cm^3 at 25˚C
Solubility in water at 25˚C:	921 g/l

III.1.5 Sodium polyacrylate

Manufacturer:	Sigma-Aldrich Co.
Density:	0.55 g/cm^3 at 25˚C
Average molecular weight:	~ 5100 (determined by gel permeation chromatography (GPC)).

III.1.6 H_2O

Type:	Ultrapure water
Purification method:	Purified by equipment “Purelab Ultra” of VWS Ltd. (U.K.)
Density:	0.9981 g/cm^3 at 25˚C

III.2 Equipments

We describe the details of the main equipments used in the study. The principals of the techniques already have been reviewed in the section of literature review.

III.2.1 Mastersizer 2000

Mastersizer 2000 (manufactured by Malvern Instruments Ltd.) was used as a laser diffraction apparatus in the study. The equipment is capable of measuring the particle size of emulsions, suspensions and dry powders. The equipment requires the samples of the emulsions and suspensions to be diluted before determining particle size. Malvern declares that the equipment can measure the particle size between 20 nm to 2000μm under certain conditions. However, during our experimental work on aqueous suspensions of $CaCO_3$, the accuracy of the results was found poor below 200 nm. The fundamental size distribution derived by the instrument is volume based. It means when the result indicates, for example, that 11% of the distribution is in the size category 6.97-7.75 microns, this means that the total volume of all particles with diameters in this range represents 11% of the total

volume of all particles in the distribution. It is important to recall that technique shows diameters of equivalent spheres. Mastersizer 2000 often introduces three sorts of diameters during reports that are briefly defined:

d (0.5): It is the size in microns at which 50% of the sample is smaller and 50% is larger in volume. This value is also known as the Mass Median Diameter (MMD) if particles have the same density.

D [4,3]: It is the volume mean diameter

D [3,2]: It is the surface area mean diameter. This is also known as the Sauter mean.

The equipment has four main parts as shown in the figure III.2:

III.2.1.1 Dispersion accessory

The purpose of a dispersion accessory is to prepare the samples and to deliver them to the optical unit for measurement. Different types of dispersion accessories may be used with Mastersizer 2000 depending upon application. In our study, we employed two dispersion accessories namely Hydro2000S and Scirocco 2000 for measuring particle size distributions of suspensions and dry powders respectively.

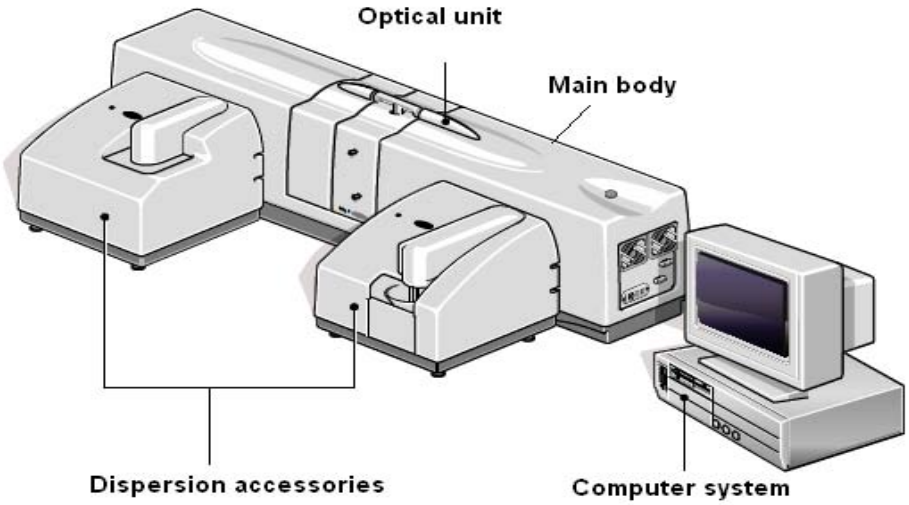

Fig. III.2: Mastersizer 2000 based upon laser diffraction technique.

III.2.1.2 Optical unit

The sample from dispersion accessories is delivered to a measurement cell built in optical unit. Two different cells namely Hydro 2000 and Scirocco 2000 were used for suspensions and dry powders respectively in the study. The laser light is passed through the sample in the cell and scattering is measured with the help of detectors built in main body.

III.2.1.3 Main body

This part contains the laser generator, focusing lens, calibrating arrangements, detectors, and other supporting arrangements.

III.2.1.4 Computer system

The Malvern software controls the system during a measurement and processes the measurement data to produce a size distribution. Its other functions are defining and controlling a measurement, displaying the results and printing reports etc. Version 5.40 of Malvern software was used in the study.

There are two basic methods of making a measurement with Mastersizer 2000 i.e. a manual measurement and a standard operating procedure (SOP) measurement. SOP's are user defined procedures that are programmed into the software to allow the same type of sample to be measured in a consistent way with all the difficult decisions on measurement strategy already having been made. When the SOP is run, it will automatically run through the defined measurement procedure, prompting the operator to perform tasks (such as adding the sample). The SOP will take full control of the accessory (except any manual accessory), making all adjustments and settings (such as pump speeds and ultrasonic power).

III.2.2 Ultrasizer

Ultrasizer (manufactured by Malvern Instruments Ltd.) was used for particle sizing in different phases of the study by acoustic attenuation spectroscopy. The technique has many advantages over other techniques of particle sizing. For example, it is non-destructive and non-invasive; it can study dispersions (suspensions and emulsions) without the need for diluting them; it can be employed online, under real process conditions, over a wide range of particle size (10 nm to 1000 μm) and over a wide concentration range (0.5% vol. to 50% vol.), depending upon application.

Malvern Ultrasizer shows a log-normal distribution that is volume based i.e. frequency of each size class in the distribution would give a volume fraction of the total particulate volume within the sample.

The main units of the Malvern Ultrasizer have been show in the figure III.3.

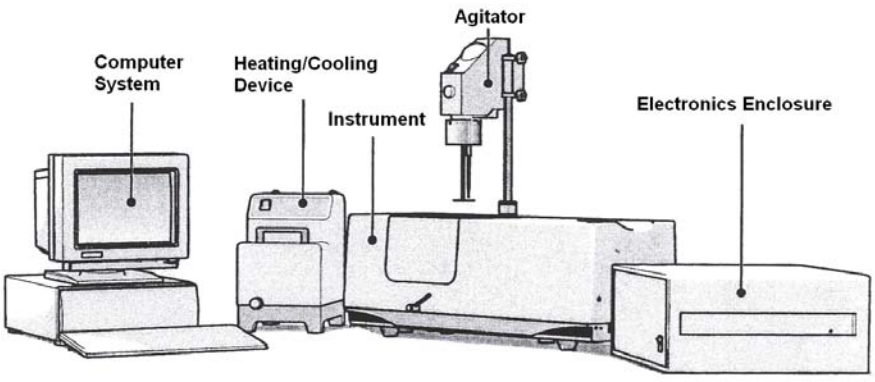

Fig. III.3: Malvern Ultrasizer

Ultrasizer can be used in two modes: (i) flow cell configuration and (ii) batch cell configuration. In two modes, different measurement cells are used. Figure III.4 (a) presents an experimental set up for measurement of particle size of a dispersion in stirred tank, under flow cell configuration. Figure III.4 (b) shows the measurement cell (in dismantled form) that is used in flow cell configuration.

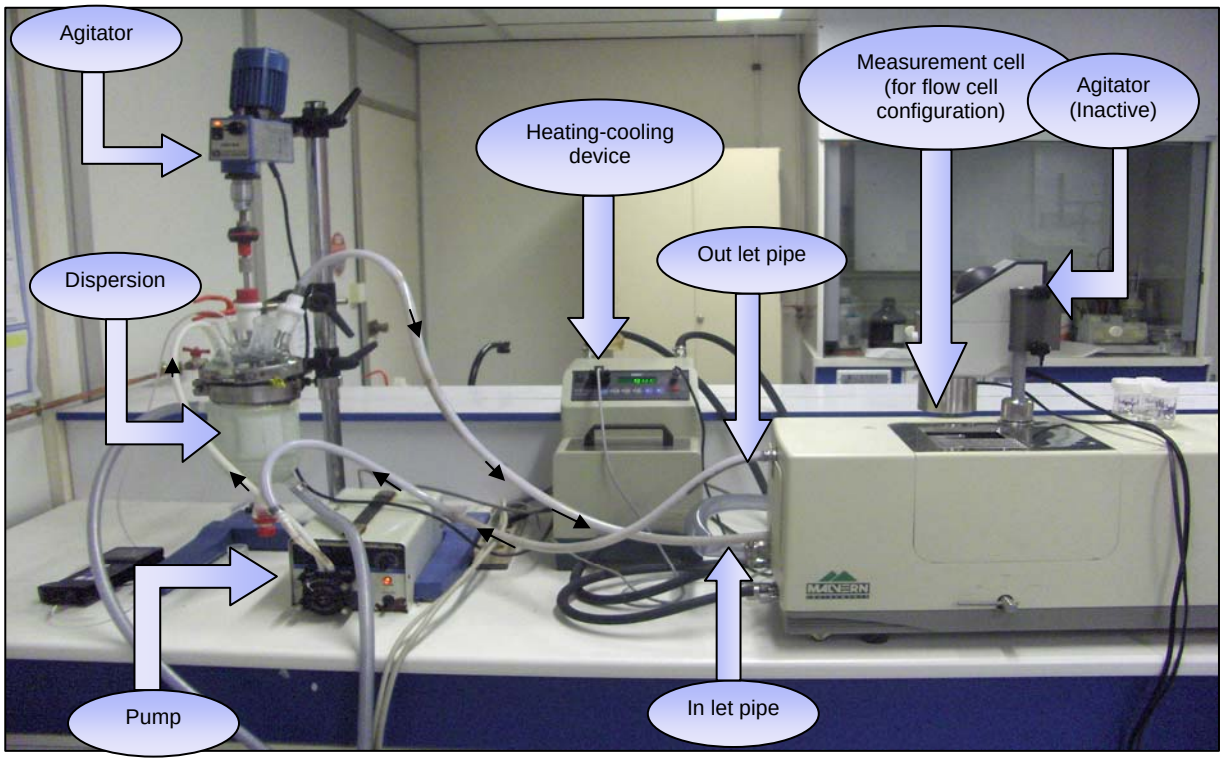

Fig. III.4 (a)

Fig. III.4 (b)

Fig. III.4: (a) Application of Ultrasizer under flow cell configuration for particle sizing of a dispersion in stirred tank (b) Measurement cell used in flow cell configuration in dismantled form.

Figure III.5 (a) presents measurement of particle size of a dispersion directly added into the batch cell of the Ultrasizer. The measurement cell used in batch cell configuration has been shown in figure III.5 (b).

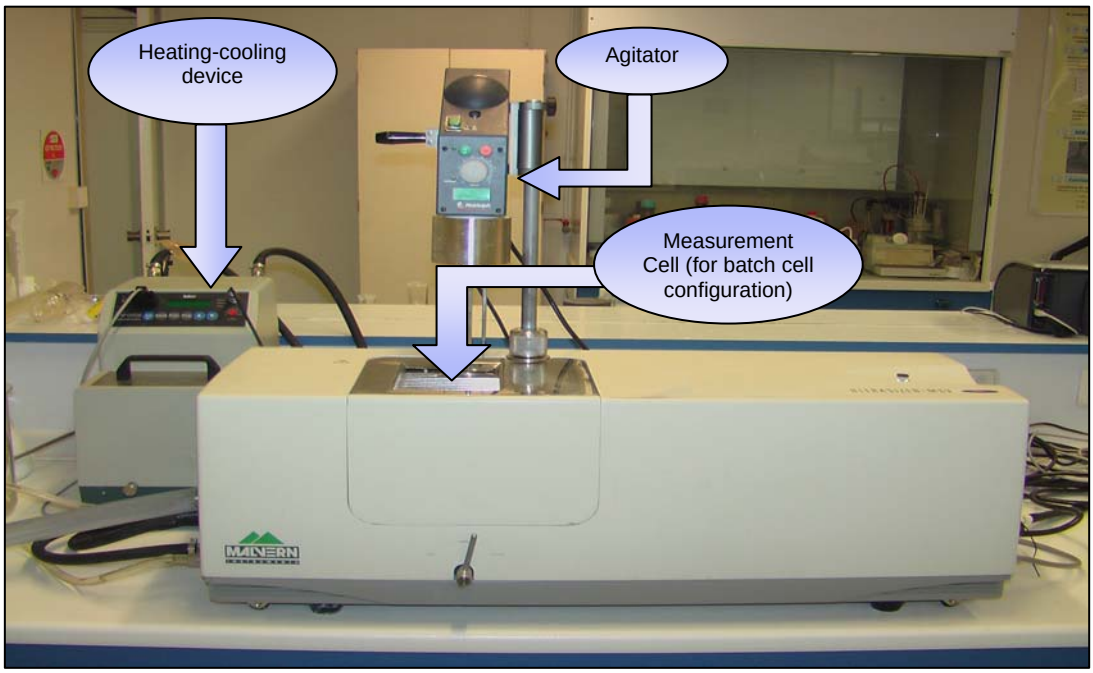

Fig. III.5 (a)

Fig. III.5 (b)

Fig. III.5: (a) Application of Ultrasizer under batch cell configuration for particle sizing of a dispersion present into the measurement cell in the instrument (b) Measurement cell used in batch cell configuration in dismantled form.

III.2.2.1 Heating/cooling device

The heating/cooling device as clear from the term is used to maintain the temperature of the dispersion at a desirable value. The water from heating/cooling device, with the help of appropriate arrangement built in Ultrasizer, enters in double jacket around the measurement cell to heat it up or cool it down in order to maintain desirable value of temperature. The heating/cooling device is controlled by the computer system in an automatic mode.

III.2.2.2 Agitator

In flow cell configuration, the agitator serves no purpose and remains inactive. However, in batch size configuration it is used to agitate the sample in the measurement cell. The speed of the agitator may be adjusted manually, according to requirements of the experiment.

III.2.2.3 Instrument

The instrument contains measurement cell (batch or flow cell) shown in figures III.4 and III.5), transducers, temperature sensor, inlet/outlet of the samples, inlet/outlet for the fluid coming from heating/cooling device, drain system, security measurements along with other supporting arrangements. Transducers are main part of the instrument and play a key role in measurement process. They are of two types: Generator and receiver. The disc on the right wall of the measurement cell contains generator transducers. They are movable and their function is to transmit continuous ultrasonic waves at controlled frequencies thought the sample to receiver transducers. In the instrument, the larger diameter disc is the low frequency transducer whereas the smaller diameter disc in the high frequency transducer. The generator transducers can be moved to vary the distance between generators and receivers according to requirement of the measurement. The disc on the left wall of the measurement cell has receiving transducers. They are fixed on the wall. They receive the ultrasonic waves after they have passed through the sample and convert these attenuated acoustic signals into electric signals which are then passed to electronic enclosure.

III.2.2.4 Electronic enclosure

The electronic enclosure provides an interface between the instrument and the computer. It contains the microwave generator and various electronic systems for amplification, for signal processing, for control of movement of transducers and for control of temperature.

III.2.2.5 Computer system

The computer system is used to run the Malvern software (Ultrasizer MSV). The software controls all the functions of the instrument during a measurement and then uses the data collected to calculate the particle size results. The particle size results are calculated on basis of ECAH theory. The physical properties of disperse and dispersion media required by the software for calculation of the particle size are listed in table III.1:

Table III.1: Physical properties required in calculation of particle size distribution	
For disperse medium:	**For dispersion medium:**
1- Density (g/cm ^{3})	1- Density (g/cm ^{3})
2- Sound velocity (cm/s)	2- Sound velocity (cm/s)
3- Thermal dilation ($^\circ C^{-1}$)	3- Thermal dilation ($^\circ C^{-1}$)
4- Thermal conductivity (erg cm^{-1} s^{-1} $^\circ C^{-1}$)	4- Thermal conductivity (erg cm^{-1} s^{-1} $^\circ C^{-1}$)
5- Heat Capacity (erg g^{-1} $^\circ C^{-1}$)	5- Heat Capacity (erg g^{-1} $^\circ C^{-1}$)
6- Shear rigidity (dynes.cm^{-2})	6- Viscosity (Poise)

In addition, the system requires the following information:

- Frequency spam for generating band of ultrasound waves
- Position of transducers

The above information is named strategy in the language of the software. There is an option in Malvern Ultrasizer to find a measurement strategy automatically in addition to other options. In Malvern Ultrasizer, the results of particle sizing can be viewed with option of mono-modal or bi-modal distribution.

III.2.3 Zetasizer nano ZS

Zetasizer nano ZS (manufactured by Malvern Instruments Ltd.) was used in the study as dynamic light scattering apparatus. The equipment is capable of measuring molecular weight and zeta potential in addition to particle size. The range of particle size that can be determined is: 0.6nm - 6µm. The equipment requires the sample to be diluted like Malvern Mastersizer 2000. The main parts of the equipment have been shown in figure III.6:

Fig. III.6: Zetasizer nano ZS

III.2.3.1 Zetasizer instrument

Zetasizer instrument contains laser generator, attenuator, detectors, and correlator besides other supporting arrangements.

III.2.3.2 Cell area

The role of cell area is important in measurement. Its important components have been shown in figure III.7. On pressing the cell access button the lid slowly raises allowing access to the cell holder. On opening, two safety interlocks (i.e. laser safety and electrode voltage) are activated for preventing laser and electrode exposure to cell. The electrodes perform two functions: (i) provide voltage for zeta potential measurements (ii) identifies if a zeta potential-cell is fitted. Depending upon the measurement to be performed, either a size or zeta potential-cell is required. When a zeta potential-cell is inserted, the electrodes positioned on either side of the cell holder enable the type of cell to be detected automatically. During the measurement the electrodes supply the voltage necessary to perform electrophoresis. The maximum working voltage on the electrodes is ±160v. If a size cell is inserted no electrode contact is made and the Zetasizer assumes a size cell is fitted. Access channel incorporated into the cell area allows sample tubes to be connected to the measurement cell.

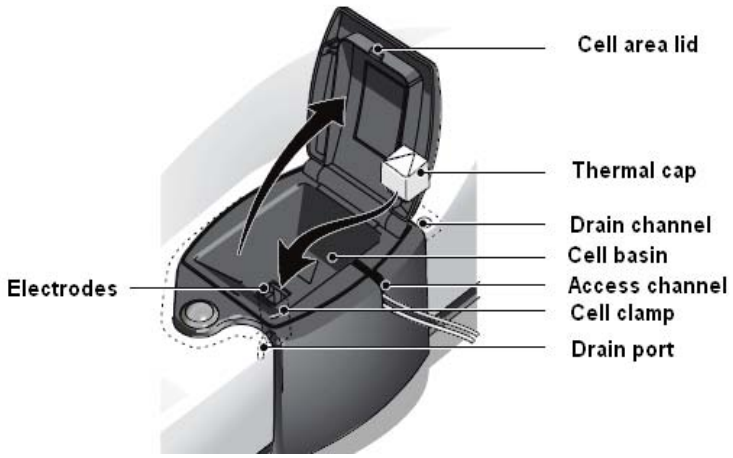

Fig. III.7: Zetasizer nano ZS: cell area

The cell basin is made of an insulating material which provides protection from the heated cell holder and in conjunction with the thermal cap gives temperature stability when heating and cooling the sample. The thermal cap gives increased temperature stability for size measurements when heating and cooling the sample during size measurements. This is important when measuring at either end of the temperature specification. The thermal cap is placed over the cell to ensure the temperature requested is reached. A parking position is provided in the cuvette holder to store the thermal cap. In case of spillage within the cell area, there is a drain incorporated into the base of the cell holder. Any spillage will exit onto the bench area underneath the Zetasizer. Likewise in case of spillage on the cover a

drainage channel is provided around the outside of the cell area, this is hidden from view under the main cover. Any spillage will flow along the drain into a hole positioned at the back of the cell area. Any spillage will exit onto the bench area underneath the Zetasizer. To keep the cell in the optimum position during a measurement, a cell clamp mechanism is incorporated into the wall of the cell holder. The clamp pushes against the edge of the cell when inserted.

III.2.3.3 Cell

Different cells may be used in the equipment depending upon the objective and measuring conditions. The standard cell and zetapotential cell as shown in the figure III.8 (a) and (b) were used respectively for measurement of particle size and zetapotential respective. Both cells were disposable and made of polystyrene. Both cell may be used up to temperature of 50˚C and require 1 ml and 0.75 ml as minimum volume of sample for measurement.

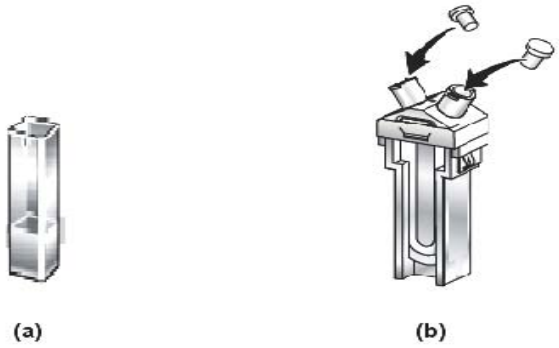

Fig. III.8: Zetasizer nano ZS: measurement cells

III.2.3.4 Computer system

Computer system uses the Malvern software for control of the equipment and for showing the results. The measurements can be made either manually or by using a standard operating procedure (SOP). A manual measurement is basically a one-off measurement where all the measurement parameters are set up immediately prior to the measurement whereas a SOP measurement uses pre-set parameters (that have previously been defined) to ensure that measurements made on the same type of sample are made in a consistent way. The important information amongst others required by the software for particle size and zetapotential measurement is: i- name of material ii- name of dispersant and iii- temperature at which measurement is to be carried out. The system takes values for refractive indexes and viscosities from the database built in the system for many materials. The detail functions of the instrument may be studied in its manual.

III.2.4 Lab Star

A lab scale stirred media mill called LabStar, manufactured by NETZSCH, was used in the study. The mill and its main parts have been shown in the figure III.9.

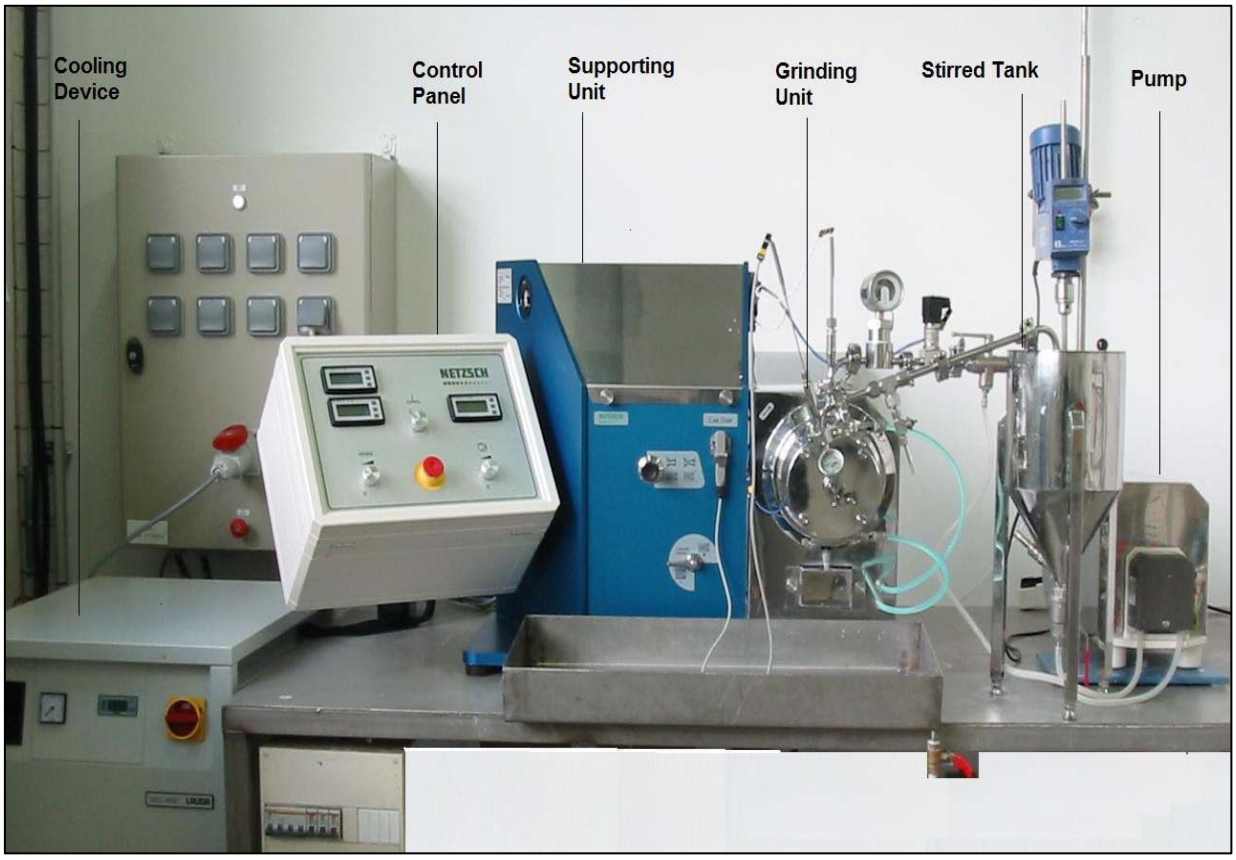

Fig. III.9: Stirred media mill: LabStar

III.2.4.1 Control panel

It is used to control the speed of agitator, speed of pump and speed of mixer. The on-off switches and display screens for speed of agitator, speed of pump, power input for agitator are also part of control panel.

III.2.4.2 Grinding unit

It is made of stainless steel and its volume is approximately 670 cm^3. In grinding unit the process of comminution takes place. The shape of stirrer that creates grinding impact has been shown in figure III.10. After experiencing a certain comminution in grinding chamber, the dispersion left through a steel (Cr-Ni-steel) separating cartridge (filter) that was installed at out let of the grinding chamber. The size of separating cartridge used in our experiments was 100 µm. The problem of contamination of the product by the materials of the mill had been reduced in the grinding unit by lining with Cr-Ni-stirred walls and equipping the agitator shaft with tungsten-carbide pegs.

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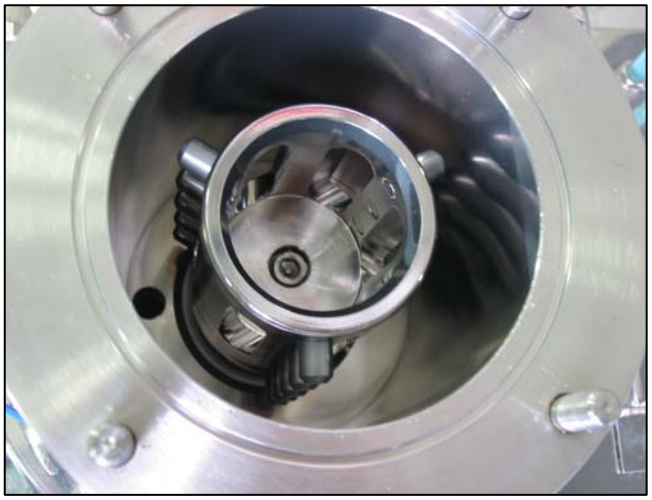

Fig. III.10: Grinding unit in disassembled form

III.2.4.3 Supporting unit

It comprises of devices such as motor for rotating agitator (stirrer) in grinding chamber, pressure reducing valve, pressure switches, cooling pipes, security valves and sealing liquid which fulfils the three tasks: (i) carrying out of frictional heat (ii) creating a lubricating film between the sliding rings (iii) sealing the mechanical seal against the product.

III.2.4.4 Pump

A peristaltic pump that is sometimes called flexible tube pump was used with LabStar. It is a type of positive displacement pump in which fluid is contained within a flexible tube fitted inside a circular pump casing. A rotor with a number of "rollers" (sometimes called shoes or wipers) attached to the external circumference compresses the flexible tube. As the rotor turns, the part of tube under compression closes (or occludes) thus forcing the fluid to be pumped to move through the tube. Moreover, as the tube opens to its natural state after the passing of the cam (restitution or resilience) fluid flow is induced to the pump. The process is named peristalsis and is used in pump of LabStar.

III.2.4.5 Stirred tank

A conical shaped stirred tank made of stainless steel is used for introducing the material (feed). An electric rotating motor with adjustable speed is mounted over the storage tank with the help of a stand for agitating the feed. The pump takes the feed from an out let at bottom of conical stirrer tank and introduces it into grinding chamber. In one pass mode of mill, feed is introduced into the stirrer tank, then enters into the grinding chamber with the help of pump and thereafter leaves as a final product. In circuit mode or multi pass mode, the feed is introduced into the grinding chamber with the help of pump, and thereafter renters into the stirrer tank to maintain a circuit mode. The conical stirred tank contains a double jacket for maintaining desirable temperature.

III.2.4.6 Cooling device

The cooling device with the help of circulating tubes around the grinding chamber removes the heat generated in grinding process. Ethylene glycol is used as a cooling medium in cooling device.

III.2.4.7 Computer system

Computer system with LabStar is a stand alone computer that controls various functions of LabStar with the help of LabDot software. It equally calculates analyses and stores the various parameters of grinding.

- Agitator speed
- Pump speed
- Product pressure
- Product temperature
- Power input of the main drive in kW
- Sum of energy input in kWh (circulation operation)
- Preselect value of the total energy input (circulation operation)

III.3 Methods

This thesis has been divided into various phases. The method adopted in each phase has been described in the respective chapter.

III.4 Reliability and precision

Malvern Ultrasizer, Malvern Mastersizer 2000 and Malvern Zetasizer Nano ZS measure the quality of each measurement during particle sizing of each sample. All the measurements reported in this work, meet the quality criterion of the equipments. Moreover, the measurements of particle sizing by laser diffraction technique, dynamic light scattering and acoustic attenuation spectroscopy have been repeated three times in order to confirm the reliability and precision of the results. All the measurements reported in this work show a reasonable reliability and precision.

Similarly, the measurements of zeta potential and determination of pH values were repeated equally three times in order to confirm the reliability and precision of the measurements.

III.5 Preliminary work

III.5.1 Determination of a single measurement strategy for acoustic measurements

One of the objectives of our study was to understand the acoustic contribution of the impurities in dispersion during particle sizing by acoustic attenuation spectroscopy (The issue is discussed in detail in chapter IV). For this, we had the following procedure in mind:

- Measuring the acoustic attenuation spectra of dispersion without impurity using a certain frequency range and certain frequency points within this range,
- Using exactly the same frequency range and frequency points to measure the acoustic attenuation spectra of the dispersion with an impurity,
- Subtracting the points of attenuations obtained in step 2 from the points of attenuations obtained in step 1 in order to get the attenuation change due to the impurity.

So, it was important in our experiments to find a single measurement strategy capable of working for all combinations of dispersions and impurities that we wanted to study. In our preliminary work, in order to find a single measurement strategy, we prepared several combinations of dispersions and impurities. We measured them again and again with several measurement strategies in order to find a single measurement strategy that could work in all cases.

Our repeated efforts, finally, led us to a desirable measurement strategy with a frequency range (1.5-10.0 MHz), transducer position 1 = 0.10 and position 2 = 0.40. In each measurement, a band of 50 different sound waves, as mentioned in table III.2, was passed through the dispersions.

Table III.2: Frequency band employed in measurements

No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)
1	1.5	11	2.2092	21	3.2537	31	4.7921	41	7.0578
2	1.5592	12	2.2964	22	3.3822	32	4.9813	42	7.3364
3	1.6208	13	2.3871	23	3.5157	33	5.1779	43	7.626
4	1.6847	14	2.4813	24	3.6545	34	5.3823	44	7.9271
5	1.7513	15	2.5793	25	3.7987	35	5.5948	45	8.24
6	1.8204	16	2.6811	26	3.9487	36	5.8156	46	8.5653
7	1.8922	17	2.7869	27	4.1046	37	6.0452	47	8.9034
8	1.9669	18	2.8969	28	4.2666	38	6.2839	48	9.2549
9	2.0446	19	3.0113	29	4.435	39	6.5319	49	9.6202
10	2.1253	20	3.1302	30	4.6101	40	6.7898	50	10

III.5.2 Determination of different acoustic trends

In our preliminary work, we have verified the suitability of acoustic attenuation spectroscopy for measuring the changes in acoustic attenuation spectra due to (1) changes in concentration of dispersion and (2) changes in proportion of particles of different sizes. For this, we prepared different dispersions of different proportions of coarse $CaCO_3$ (30 µm) and relatively fine $CaCO_3$ (1.6µm), as mentioned in table III.3. The acoustic attenuation spectra were measured with the help of measurement strategy mentioned in above section.

Table III.3: Aqueous dispersions of $CaCO_3$ mixed with different proportion of coarse and relatively fine particles.

Dispersion No.	H_2O Ca	CO_3 (30 µm)	$CaCO_3$ (1.6 µm)	Total solid concentration (%)
	g	g	g	(mass of $CaCO_3$ /total mass of suspension)
(1)	700	200	0	22.22
(2)	700	0	5	0.71
(3)	700	0	25	3.45
(4)	700	0	50	6.66
(5)	700	0	100	12.50
(6)	700	0	150	17.65
(7)	700	200	5	22.65
(8)	700	200	25	24.32
(9)	700	200	50	26.31
(10)	700	200	100	30.00
(11)	700	200	150	33.33

The comparison of acoustic attenuation spectra of dispersions (3) to dispersions (6), as in figure III.11, explains that acoustic attenuation spectra rise with increasing concentration of the dispersions.

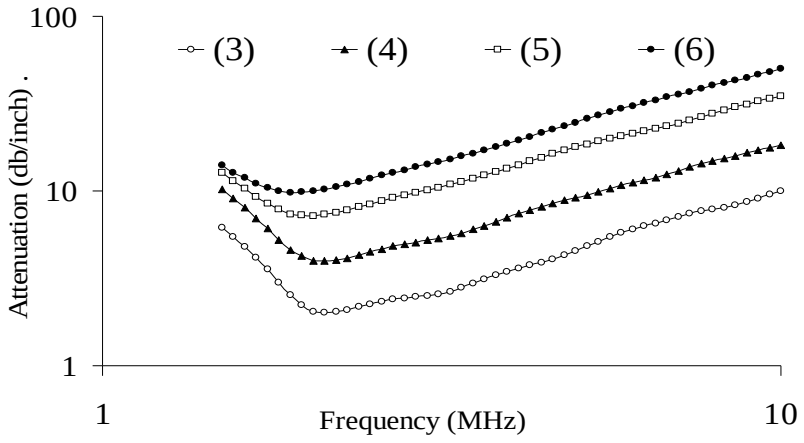

Fig. III.11: Changes in acoustic spectra with increasing concentration of the dispersion.

The technique is capable of finding the changes in concentration of the dispersions. In the figure III.11, the acoustic attenuation spectrum of dispersion (2) was not plotted. The acoustic attenuation spectroscopy is not suitable for very dilute dispersion such as dispersion (2) of 0.7% (m/m). At very lower concentration, the number of particles present in a sample are not sufficient. The possibility of interaction between sound waves and particles is reduced significantly and the measurements are not reliable. The limit of dilution may be different in different systems particularly depending upon size of the particles. In our experiments, the minimum workable concentration of the dispersions seems to be 1% (m/m).

Similarly, in order to understand the effects of small increase in the proportion of relatively fine particles, the acoustic attenuation spectra of dispersions (7) to (11) were compared. It was observed that the acoustic technique is capable of distinguishing between the dispersions with different proportions of finer particles as shown in figure III.12.

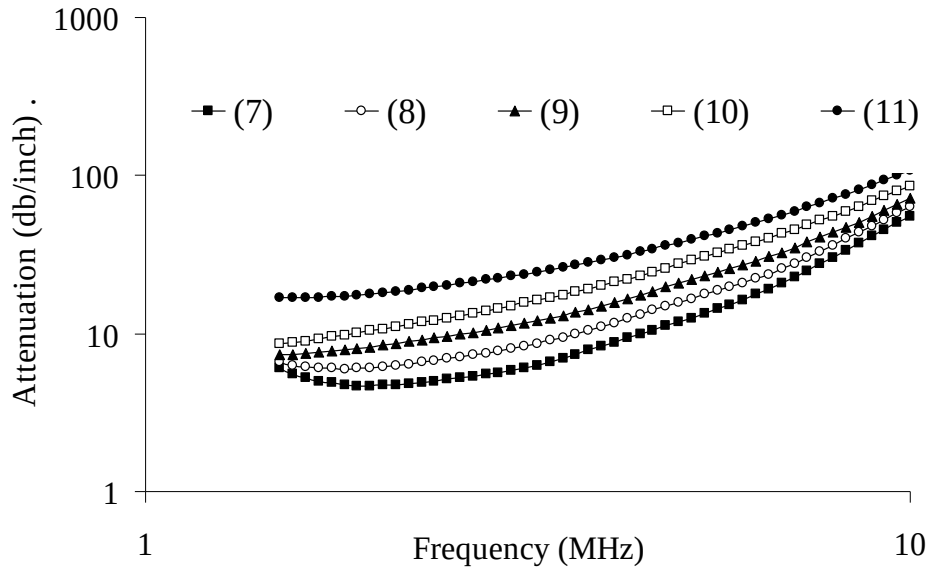

Fig. III.12: Changes in acoustic spectra with increasing proportion of fine particles in dispersion.

These preliminary results establish that acoustic attenuation spectroscopy will be capable of characterizing the size reduction process in which a similar scenario is experienced. i.e. (i) high concentrations of the dispersions, (i) poly dispersity in the particles and (iii) increase in the proportion of fine particles with increasing grinding time.

Pour conclure

Ce chapitre constitue en quelque sorte une annexe technique par rapport aux chapitres suivants IV, V, et VI qui constitueront le cœur de la thèse. Il rassemble quelques données physiques sur les produits qui seront utilisés par la suite et il synthétise un certain nombre de données techniques sur les appareils de caractérisation et sur le dispositif de broyage qui serviront de base aux essais expérimentaux.

La mise en œuvre de la technique de spectroscopie acoustique étant relativement délicate, nous avons également rapporté dans ce chapitre quelques résultats de mesures préliminaires. Le résultat d'une mesure de spectroscopie acoustique s'exprime sous la forme d'un spectre d'atténuation acoustique, qui représente l'atténuation d'une onde sonore au passage du milieu dispersé en fonction de la fréquence de cette onde incidente. Des mesures du spectre d'atténuation ont été réalisées pour des suspensions de carbonate de calcium de différentes concentrations et/ou en mélangeant en proportions connues deux lots de carbonate de calcium présentant des tailles moyennes caractéristiques différentes. Nous avons observé d'une part que l'atténuation acoustique augmente de manière significative lorsque la concentration en solide augmente. D'autre part, la technique est également sensible à une augmentation dans la dispersion de la proportion de fines particules. Des concentrations importantes en solide ne semblent pas perturber l'analyse de l'atténuation acoustique ; les spectres obtenus sont tout à fait exploitables pour des concentrations allant au moins jusqu'à 33% (masse de carbonate de calcium/masse de suspension). Nous n'avons pas cherché à considérer des suspensions plus concentrées en carbonate de calcium, car en l'absence d'agent dispersant, les suspensions aqueuses de carbonate de calcium s'agrègent et ne sont plus homogènes. Par ailleurs, nous avons observé que la spectroscopie acoustique n'est pas adaptée à la mesure de suspensions diluées. Il est nécessaire que le milieu contienne un nombre significatif de particules pour que l'onde sonore le traversant entre le générateur et le récepteur soit atténuée. La concentration minimale avoisine les 1% (g/g suspension).

Les résultats de ces essais préliminaires seront repris et commentés plus largement dans le chapitre V.

Effects of Impurities on Particle Sizing by Acoustic Attenuation Spectroscopy

** As per requirements of the university, a preface in the beginning and concluding remarks at the end of the chapter have been given in French.*

Préface en français

Pour de nombreux procédés industriels mettant en œuvre des particules en suspensions concentrées, il est important d'avoir des données précises sur la distribution de taille des particules pour le contrôle de ces procédés ou pour l'optimisation de leurs conditions de fonctionnement. Or, le suivi de la distribution de taille de particules en ligne des procédés et sous des conditions réelles d'écoulement pour les procédés impliquant des dispersions (suspension et émulsions) concentrées n'est pas facile à réaliser. Dans ce contexte, les méthodes acoustiques semblent une voie prometteuse. Toutefois, l'analyse de la bibliographie a révélé que cette technique a encore besoin d'être étudiée parce qu'on ne sait pas exactement comment et sous quelles conditions elle peut être utilisée lorsque les dispersions comportent des impuretés ou des additifs solubles ou insolubles. Avant d'analyser l'apport de cette technologie au suivi d'un procédé de broyage en voie humide, ce chapitre vise à préciser les conditions d'application de la spectroscopie acoustique pour la caractérisation de milieux denses contenant différents types d'impuretés et dans une gamme de concentration relativement étalée.

Ce chapitre a fait l'objet d'une publication acceptée dans J. of Powder Technology. Il est reproduit ici dans son intégralité. Des données complémentaires qui n'apparaissent pas dans la publication mais qui ont été utilisées lors de sa rédaction figurent en Annexes à la fin du mémoire.

IV. Effects of Impurities on Particle Sizing by Acoustic Attenuation Spectroscopy

This chapter has been published in the journal of Powder Technology.
Paper title: Effects of impurities on particle sizing by acoustic attenuation spectroscopy.
Reference: Powder Technology 201 (2010) 21–26

Abstract: It is important to have correct information regarding particle size in order to interpret, control, and optimize many industrial processes. Prior to the recent advent of acoustic attenuation spectroscopy, it was difficult to study particle size distribution online and under real process conditions in processes involving concentrated dispersions (suspensions or emulsions). The technique still needs improvement because it is less known how and under which conditions to employ the technique when dispersions involve impurities that could be soluble, insoluble, in the form of additives, and so on. This lack of understanding has almost halted the advancement in applications of the technique to various processes that essentially involve dispersions with impurities. This study investigates aqueous suspensions of $CaCO_3$ at different concentrations (i.e., 5%, 10% and 20% mass/mass) with added impurities of $MgCO_3$ (insoluble impurity), $NaNO_3$ (soluble impurity) and sodium polyacrylate (soluble additive) at varying proportions (5%, 10%, 20% and 30% of the weight of $CaCO_3$). The study characterizes and compares dispersion with and without impurity in order to demonstrate the possible ways in which addition of an impurity change the original acoustic attenuation spectrum of a dispersion. The study brings the conditions in which acoustic attenuation spectroscopy is capable of explaining that addition of an impurity will not change original particle size of the disperse medium.

Keywords: Acoustic attenuation spectroscopy, dispersions, impurities, particle sizing.

IV.1 Introduction

It is important to have correct information regarding particle size in many industries such as chemicals, paints, dyes, pharmaceuticals and cosmetics in order to interpret, control, and optimize many processes. In last few decades, many techniques of particle sizing have been developed based on different principles such as laser diffraction, dynamic light scattering, image analysis and acoustic attenuation spectroscopy. Each technique has its advantages and limitations depending upon the application. In above techniques, acoustic attenuation spectroscopy is quite prominent because of many advantages over other techniques of particle sizing. For example, it is non-destructive and non-invasive; it can study dispersions (suspensions and emulsions) without the need for diluting them; it can be employed online, under real process conditions, over a wide range of particle size (10 nm to 1000 μm) and over a wide concentration range (0.5 vol % to 50 vol %), depending upon application (Dukhin 2001a, 2001b,Alba et al., 1999, Challis et al., 2005, McClements, 2000). Many studies have verified suitability of acoustic attenuation spectroscopy for simple dispersions (i.e. dispersion involving one disperse phase and one continuous phase). However, there is still lack of understanding how and under which conditions to employ the technique when dispersions are not simple. For example, in many industrial applications, dispersion of $CaCO_3$ are prepared from raw $CaCO_3$ that may contain impurities such as silica or $MgCO_3$ making the dispersion of $CaCO_3$ complex for particle sizing by means of acoustic attenuation spectroscopy. Similarly, during wet grinding processes, the addition of additives in dispersions makes them complex. The lack of understanding has almost halted the advancement in applications of the technique to various processes that essentially involve dispersions with impurities etc. Pointing out this lack, Franck Babick et al. (2000) write that only little experience has been gained for the performance under more real conditions, e.g. for the presence of contamination, for multi-component-systems or for the case that the knowledge of the involved phases is incomplete. Similarly, Povey (2006) has emphasized the importance of characterizing the surfactants in the solvent for successful particle sizing by means of acoustic attenuation spectroscopy. This study is an attempt to bridge the gap between particle sizing of the dispersion with and without impurities by means of acoustic attenuation spectroscopy. In particular, the study aims to characterize and compare dispersions with and without impurities at different conditions in order to find possible conditions in which dispersions with impurities may be studied by means of acoustic attenuation spectroscopy.

IV.2 Theory

Particle sizing by means of acoustic attenuation spectroscopy is based mainly upon ECAH theory, which is presented in terms of differential waves equations derived from fundamental laws of conservation of mass, energy, momentum, thermodynamic equations of state and stress-strain relations for isotropic elastic solids (or viscous fluids). It considers case of simple dispersions (one disperse

medium in one continuous phase). The details of ECAH theory may be studied in the papers of Epstein and Carhart (1953) and Allegra and Hawley (1972) who contributed to development of this theory. With the help of ECAH theory, acoustic attenuation spectrum of a dispersion can be determined if particle size distribution and certain physical properties of the dispersion are known. The figure IV.1 (a) illustrates a simple schematic of ECAH in terms of input and output. A commercial acoustic attenuation spectrometer for particle sizing (such as Malvern Ultrasizer) makes use of ECAH theory in a manner as illustrated in figure IV.1 (b).

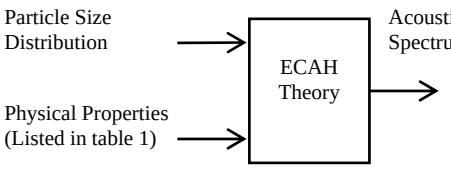

Fig. IV.1 (a)

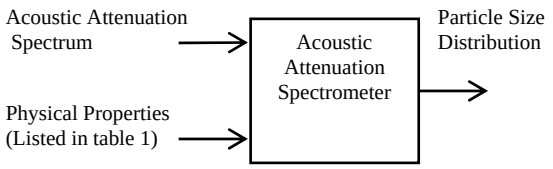

Fig. IV.1 (b)

Fig. IV.1: (a) Schematic of ECAH theory in terms of input-output. (b) Schematic of an acoustic attenuation spectrometer in terms of input-output.

It measures acoustic attenuation spectrum with the help of transducers; use information of physical properties (mentioned in table IV.1) and finally determines particle size distribution by inverse calculations. The process of inverse calculations is carried out with suitable algorithms employed generally with the help of computer program.

Table IV.1: Physical properties required for particle sizing by acoustic attenuation spectroscopy

Disperse medium (particles)	**Dispersing or continuous medium**
1- Density (g/cm ^{3})	1- Density (g/cm ^{3})
2- Sound velocity (cm/s)	2- Sound velocity (cm/s)
3- Thermal dilation ($^\circ C^{-1}$)	3- Thermal dilation ($^\circ C^{-1}$)
4- Thermal conductivity (erg cm^{-1} s-1 $^\circ C^{-1}$)	4- Thermal conductivity (erg cm-1 s^{-1} $^\circ C^{-1}$)
5- Heat Capacity (erg g^{-1} $^\circ C^{-1}$)	5- Heat Capacity (erg g^{-1} $^\circ C^{-1}$)
6- Shear rigidity (dynes. cm^{-2})	6- Viscosity (Poise)

When a sound wave of certain frequency is passed through a particulate system, it interacts with the particles (transmission, reflection, absorption and scattering etc.) and as a result it undergoes attenuation (decrease in amplitude) that can be measured in terms of attenuation coefficient (Dukhin, 2001a, 2001b; Alba et al., 1999; Challis et al., 2005; McClements, 2000). It is defined as decrease in the amplitude of the sound wave per unit distance travelled and may be expressed as (McClements, 2000):

$$\alpha = -\frac{1}{x}\ln\frac{A_x}{A_0} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$

Where A_0 is the initial amplitude of the sound wave (x=0) and A_x is the amplitude after it has travelled a distance x as illustrated in figure IV.2.

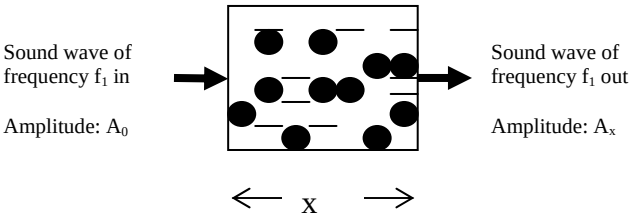

Fig. IV.2: Passage of a sound wave through a dispersion.

If a band of sound waves of different frequencies is passed through a dispersion from a certain distance (x), the attenuations in each sound wave of certain frequency may be calculated using equation 4.1. An acoustic attenuation spectrum describes acoustic attenuation constants expressed as a function of respective frequencies of sound waves. In a commercial acoustic attenuation spectrometer such as Malvern Ultrasizer, different values of x and range of frequencies may be selected for determining an acoustic attenuation spectrum. Alba discussed the relationship between frequency, attenuation constant and particle size distribution by means of acoustic attenuation spectroscopy (Alba et al., 1999). If the attenuation is measured at a single frequency, there would be four potential monosize distributions, which could have produced that measured attenuation: two in the region of viscous attenuation, one in the Rayleigh scattering region, and a fourth in the diffraction zone. In the absence of either measurement or modeling errors, two frequencies would suffice to identify the correct size from the four possible sizes for each frequency.

IV.3 Materials

$CaCO_3$: $CaCO_3$, procured through Merck KGaA Germany, served as the disperse medium in the study. It was prepared by precipitation and had the following properties: density at 20˚C = 2.93 g/cm^3, bulk density ~ 400-700 kg/m^3, solubility in water at 20˚C = 0.014 g/l, and thermal decomposition > 825˚C. A Mastersizer2000 of Malvern Instruments Limited, U.K., which is based on laser diffraction technique, was used to find the mean particle size of $CaCO_3$ (in dry form). It was found to be 1.6 µm.

Magnesium carbonate: Magnesium Carbonate (anhydrous) was purchased from Fisher Scientific, U.K. It was insoluble in water and its density was 2.958 g/cm^3 at 25˚C. Its mean particle size (in dry form) was determined by using the laser diffraction technique with a Mastersizer2000 of Malvern Instruments Limited, U.K. It was found to be 7.3 µm.

Sodium nitrate: Sodium nitrate was purchased from Fisher Scientific, U.K. Its density was 2.26 g/cm^3 It was highly soluble in water with a solubility 921 g/l at 25˚C.

Sodium polyacrylate: Sodium polyacrylate procured through Sigma-Aldrich Co. was used in the study. It had a density of 0.55 g/cm^3 at 25˚C and average M_w ~ 5100 (determined by gel permeation chromatography (GPC)).

H_2O: Ultrapure water produced from "Purelab Ultra" of VWS Ltd. (U.K.) was used in the study. The density of water was found to be 0.9981 g/cm^3 at 25˚C.

IV.4 Equipment and software

An acoustic attenuation spectrometer (Ultrasizer) of Malvern Instruments Limited U.K. was employed in the study. The system has four main units: (i) Instrument (ii) Electronics enclosure (iii) Heater/chiller (iv) Computer system. The instrument uses transducers to pass ultrasonic waves through a sample of dispersion. The sample may be measured in batch or continuous mode. The electronic enclosure contains the microwave generator and various electronic systems for amplification, for signal processing, for control of movement of transducers and for control of temperature. The heater/chiller was used to control the temperature. The computer system is a standalone computer to run the Malvern software (Ultrasizer MSV) to control the equipment. In Malvern Ultrasizer, selection of an appropriate measurement strategy (selected value of x and frequency range) is an important step. In our study, we wanted to calculate the acoustic contribution of the impurities for which it was important to measure all the combinations of dispersions and impurities with a single measurement strategy. Repeated efforts, finally, led us to a desirable measurement strategy with a frequency range of 1.5-10.0 MHz, transducer position 1 = 0.10 and position 2 = 0.40. In each measurement, a band of 50 different sound waves, as mentioned in table IV.2, was passed through the dispersions.

Table IV.2: Frequency band employed in the measurements

No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)	No.	Frequency (MHz)
1	1.5	11	2.2092	21	3.2537	31	4.7921	41	7.0578
2	1.5592	12	2.2964	22	3.3822	32	4.9813	42	7.3364
3	1.6208	13	2.3871	23	3.5157	33	5.1779	43	7.626
4	1.6847	14	2.4813	24	3.6545	34	5.3823	44	7.9271
5	1.7513	15	2.5793	25	3.7987	35	5.5948	45	8.24
6	1.8204	16	2.6811	26	3.9487	36	5.8156	46	8.5653
7	1.8922	17	2.7869	27	4.1046	37	6.0452	47	8.9034
8	1.9669	18	2.8969	28	4.2666	38	6.2839	48	9.2549
9	2.0446	19	3.0113	29	4.435	39	6.5319	49	9.6202
10	2.1253	20	3.1302	30	4.6101	40	6.7898	50	10

IV.5 Fitness of the measurements

Figure IV.1 (b) explains that process of determination of particle size depends upon: (i) physical properties of dispersion and (ii) acoustic attenuation spectrum. For right particle sizing, the acoustic attenuation spectrum must be measured with reasonable accuracy. The fitness of an acoustic

attenuation spectrum (i.e. attenuation constants vs. frequencies) depends upon accuracy of measurement of attenuation constants. In Malvern Ultrasizer, the fitness of an acoustic attenuation spectrum is measured by a parameter “spectral quality” which depends upon measurement strategy (i.e. selected value of x and frequency range). A spectral quality less than 5 indicates that the attenuation constants have been measured with reasonable accuracy. All measurements reported in this study had a spectral quality less than 5.

IV.6 Experiments

The experiments were designed to sequentially study the effects of three different impurities (magnesium carbonate (insoluble), sodium nitrate (soluble) and sodium polyacrylate (additive)) added to different aqueous dispersions of $CaCO_3$ (5% m/m, 10% m/m and 20% m/m) in the proportions 5%, 10%, 20% and 30% of the weight (mass) of the disperse medium ($CaCO_3$). The notation m/m represents mass of $CaCO_3$ divided by sum of masses of $CaCO_3$ and water.

In all experiments, dispersions of $CaCO_3$ in water were prepared directly in the batch measurement cell of the acoustic equipment (Malvern Ultrasizer) at 25˚C and at an agitator speed of 1800 rpm. Mixtures of impurities in dispersions were evaluated at the same conditions of temperature and agitation speed.

The following is a detailed description of one case for elaboration of the procedure. Consider the case of 5% m/m dispersion of $CaCO_3$ in water that was contaminated with different concentrations of magnesium carbonate. First, 500.0 ± 0.1 g water was added to the batch measurement cell of the acoustic instrument (Malvern Ultrasizer), followed by 26.32 ± 0.1 g of $CaCO_3$. Both were mixed for 20 minutes in the measurement cell at 25˚C and at 1800 rpm, followed by the first acoustic measurement. After 10 minutes, another acoustic measurement was taken under the same conditions. The second acoustic measurement was compared with the previous one. The similarity in the results of the two acoustic measurements convinced us of the homogeneity of the dispersion. In the cases where two measurements were not found to be similar, we considered the system to be inhomogeneous. It was further mixed until achievement of homogeneity. After confirmation of homogeneity of the dispersion of $CaCO_3$, 1.32 ± 0.1 g of magnesium carbonate (i.e., 5% of the weight of the disperse medium) was added to the dispersion. The system was further mixed until it again became stable and homogeneous. The stability and homogeneity were confirmed by the procedure described above. The concentration of magnesium carbonate was increased to 10% of the weight of the disperse medium by a further addition of 1.32 ± 0.1 g of magnesium carbonate into the system. Acoustic measurement was repeated upon achievement of stable and homogenized state. Similarly, the concentration of magnesium carbonate was increased to 20% of the weight of the disperse medium by adding 2.63 ± 0.1 g magnesium carbonate into the system. Acoustic measurement was repeated during the stable and homogenized phase as mentioned above. The process was repeated by increasing the concentration of

magnesium carbonate to 30% of the weight of the disperse medium. The same procedure was adopted in all other experiments.

IV.7 Results and discussions

IV.7.1 Effects of concentration of dispersions on acoustic attenuation spectra

A comparative approach was used to study the effects of concentration of the dispersion of $CaCO_3$ on acoustic spectra in the absence and in the presence of certain proportions of impurities.

IV.7.1.1 Dispersions without impurities, contaminations or additives

Our experiments revealed that in this case, acoustic attenuation spectra rise with increase in concentration of dispersion, as shown in an example in figure IV.3(a).

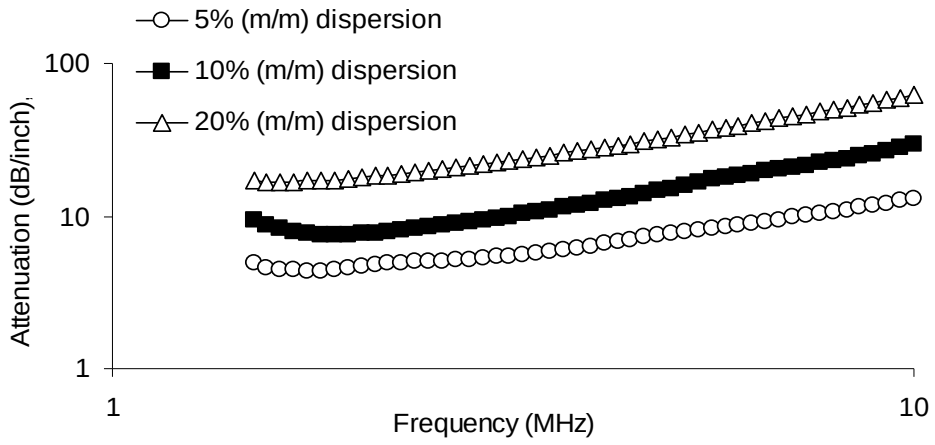

Fig. IV.3(a)

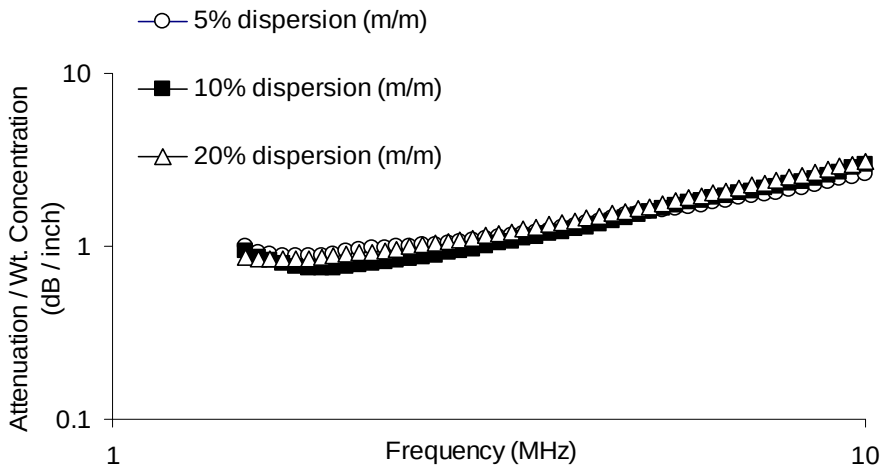

Fig. IV.3(b)

Fig. IV.3: (a) Attenuation spectra of dispersions of Calcium Carbonate without addition of impurities. (b) Attenuation spectra of dispersions of Calcium Carbonate (without impurity) divided by respective weight concentrations.

In order to confirm whether the two factors (i.e., attenuation and concentration of dispersion) are directly proportional, the attenuation values were divided by the respective values of concentrations. All three attenuation spectra were almost superimposed, indicating a proportional relationship between attenuation and concentration of dispersion, as shown in figure IV.3(b).

A slight irregularity in the first portion of the graphs in figures IV.3(a) and IV.3(b) may be due to operational incapability (higher signal to noise ratio) of the equipment that usually occurs at the beginning of an acoustic measurement. A possible explanation of the phenomenon of superimposition, as observed in figure IV.3(b), could be that at a given concentration of the dispersion, each particle (or aggregate) had a certain average size and a certain acoustic attenuation corresponding to that size. Total acoustic attenuation of the dispersion was the sum of acoustic attenuation of all particles (or aggregates). Every increase in the concentration of the dispersion added more particles (or aggregates) of same average size. These particles (or aggregates) retained their size; in other words, they did not interact to form bigger particles (flocs or aggregates). Therefore, the total acoustic attenuation increased proportionally to the number of particles (or aggregates), or in other words, proportionally to the concentration of the dispersion. The situation leads to the following conclusions:

- The particles of the same average size are added to the dispersion,
- The addition of particles (i.e. increase in concentration) does not lead to change in average particle size of the dispersion (absence of beginning of aggregation or de-aggregation etc.) and
- The addition of particles does not cause to start multiple scattering.

IV.7.1.2 Dispersion with impurities, contaminations or additives

As in section IV.7.1.1, the effects of concentration of dispersions of $CaCO_3$ (5%, 10% and 20% m/m) on acoustic spectra were studied by adding the impurity $MgCO_3$ in the amounts of 5%, 10%, 20% and 30% of the $CaCO_3$ used. Similar experiments were performed using the impurity sodium polyacrylate, and later on impurity $NaNO_3$. Overall, three trends are found:

(i) Acoustic attenuation spectra rise proportionally with increasing concentrations of the dispersion (the same trend as in section IV.7.1.1). Please see figures IV.4(a) and IV.4(b) as an example[*].

(ii) Acoustic attenuation spectra rise, but non-proportionally, with increasing concentrations of the dispersion. Figures IV.5(a) and IV.5(b) demonstrate this[†].

(iii) Acoustic attenuation spectra do not show a definable relationship with concentrations of the dispersion. Figures IV.6(a) and IV.6(b) demonstrate this.

[*] *Supplementary results may be studied in appendix A at the end of this manuscript.*

[†] *Supplementary results may be studied in appendix B at the end of this manuscript.*

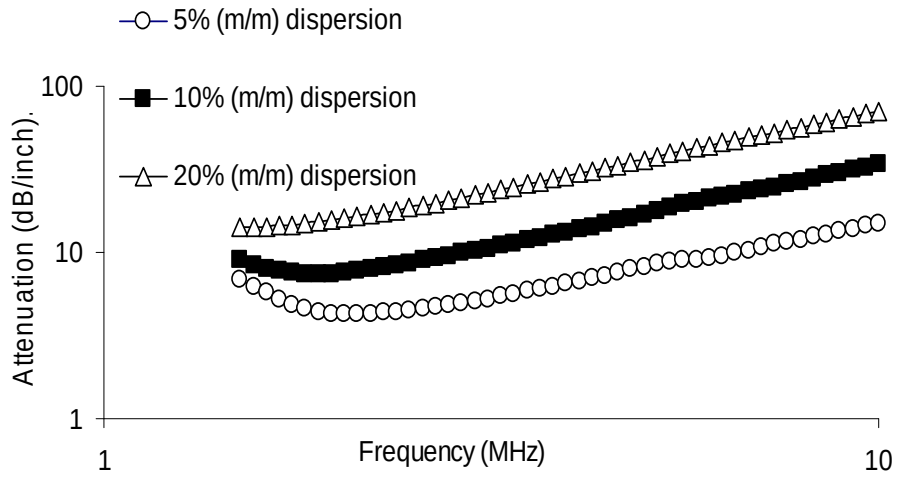

Fig. IV.4(a)

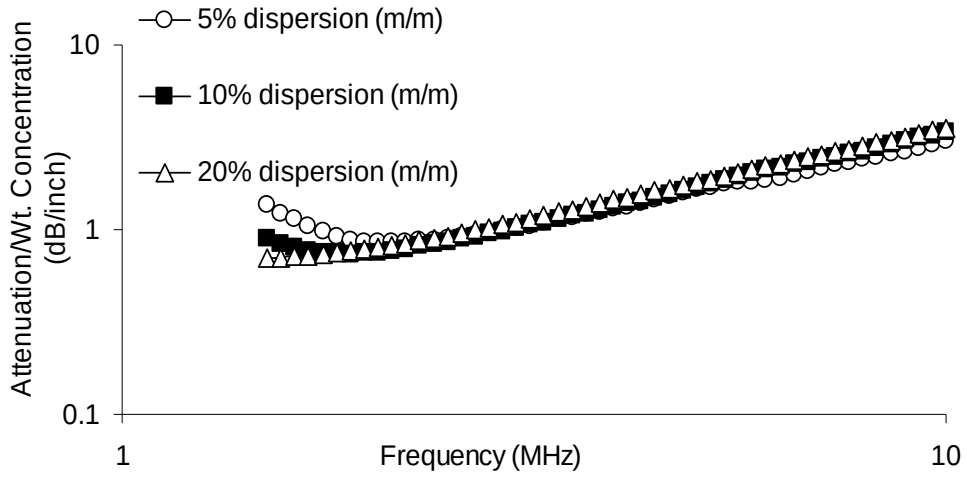

Fig. IV.4(b)

Fig. IV.4: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 10% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 10% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity.

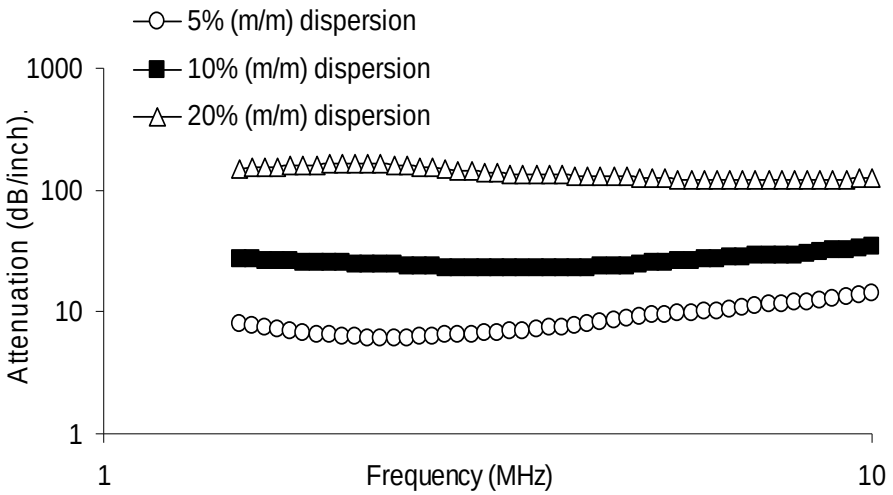

Fig. IV.5(a)

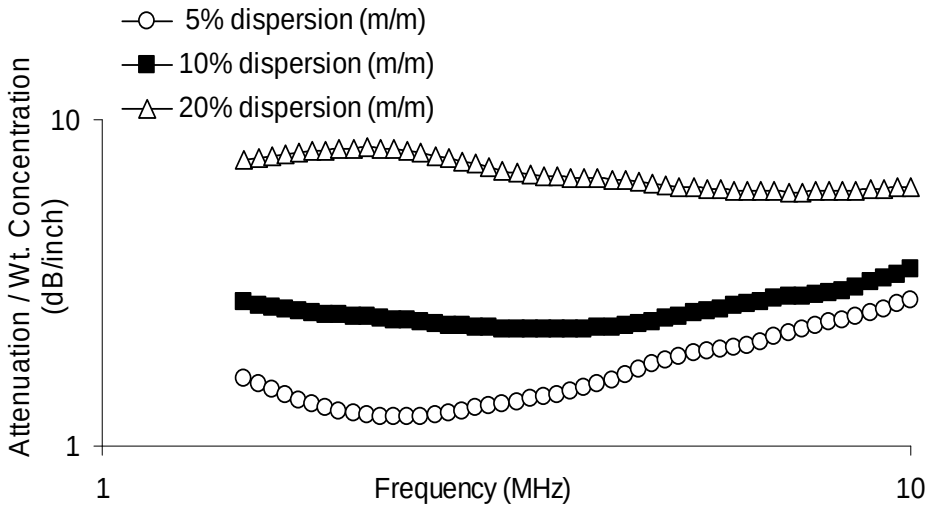

Fig. IV.5(b)

Fig. IV.5: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 30% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 30% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity.

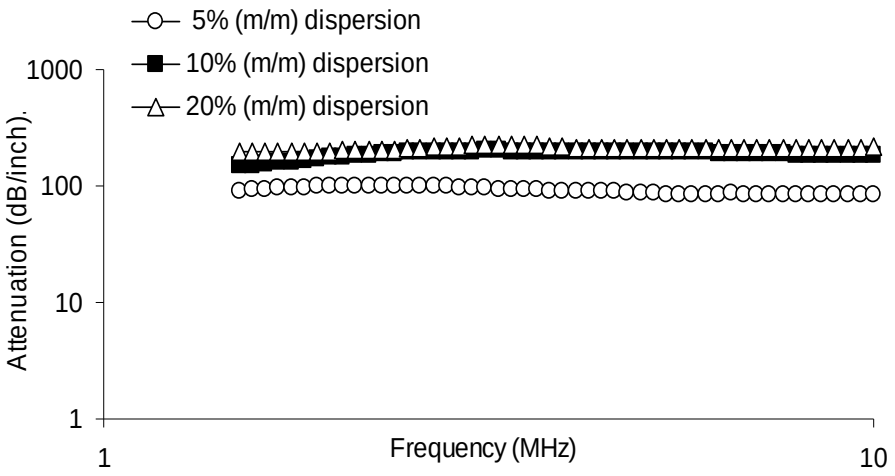

Fig. IV.6(a)

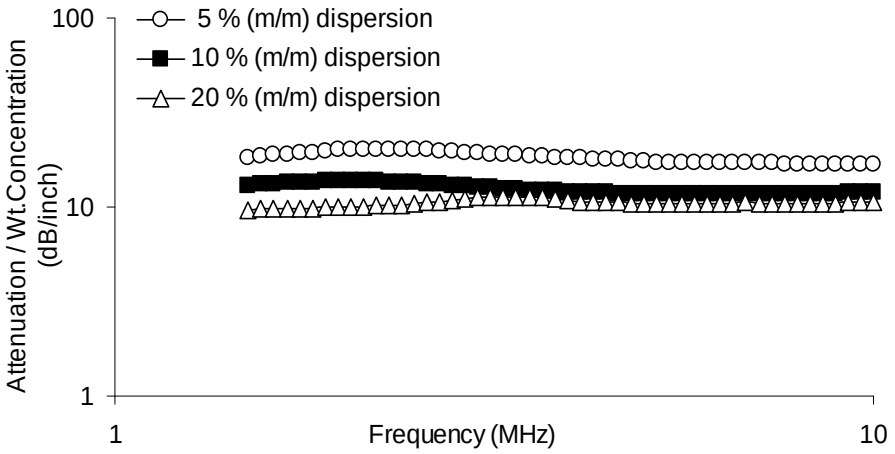

Fig. IV.6(b)

Fig. IV.6: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 30% Sodium Polyacrylate of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 30% Sodium Polyacrylate of the weight of $CaCO_3$ is present as impurity.

The conditions leading to the three trends are summarized as follows.

Trend 1: The dispersions of $CaCO_3$ follow trend 1 in the presence of the impurity magnesium carbonate (in all proportions: 5%, 10% 20% and 30% by weight of the disperse medium). Similarly, the dispersions of $CaCO_3$ follow the trend 1 in the presence of impurity $NaNO_3$ (only in proportions of 5% and 10%). Trend 1 is similar to the trend observed in section IV.7.1.1; hence, the conclusions drawn in section IV.7.1.1 may be equally applied to all combinations of the dispersions and impurities falling under this trend. The approach opens a way to study dispersions with impurities using acoustic attenuation spectroscopy.

Trend 2: The dispersions of $CaCO_3$ follow trend 2 in the presence of the impurity $NaNO_3$ (in proportions of 20% and 30%). Similarly, trend 2 is observed in case of the impurity sodium polyacrylate (in proportions of 5%, 10% and 20%). Trend 2 is characterized by a non-proportional increase in acoustic spectra with concentration. There are many possible explanations for this tendency, such as the beginning of formation of aggregates or flocs between particles, between particles and the impurity or between the impurity, or the beginning of multiple scattering, etc.

Trend 3: This was observed in presence of the impurity sodium polyacrylate in the proportion of 30%. The trend was found to be complex in nature. The likely causes could be de-aggregation or multiple scattering that appear at a certain combination of concentrations of dispersion and dispersant.

IV.7.2 Effects of concentration of impurities on acoustic attenuation spectra

This section analyzes the effect of an increase in concentration of an impurity on attenuation spectra of a dispersion at a given concentration. Several combinations were studied. It was found that under some conditions, the rise of attenuation spectra was proportional to the amount of the added impurity. Figure IV.7(a) shows the effects of different concentrations (proportions) of the impurity $NaNO_3$ on a 10% (m/m) dispersion of $CaCO_3$[‡]**.** In order to study the relationship between the change in spectra and the concentration of the impurity, the following method was adopted.

In all experiments, attenuation values of a pure dispersion were subtracted from attenuation values of the relevant impure dispersion to obtain the attenuation change due to the total quantity (%age) of impurity. This value was divided by the total quantity (%age) of impurity, and the results were plotted against corresponding frequencies to get attenuation spectra based on unit impurity. If attenuation spectra per unit impurity superimpose, then we can quantify the effects contributed by that impurity to the total acoustic attenuation spectra under given conditions. Figure IV.7(b) presents an example[§].

[‡] *Supplementary results may be studied in appendix C at the end of this manuscript.*
[§] *Supplementary results may be studied in appendix D at the end of this manuscript.*

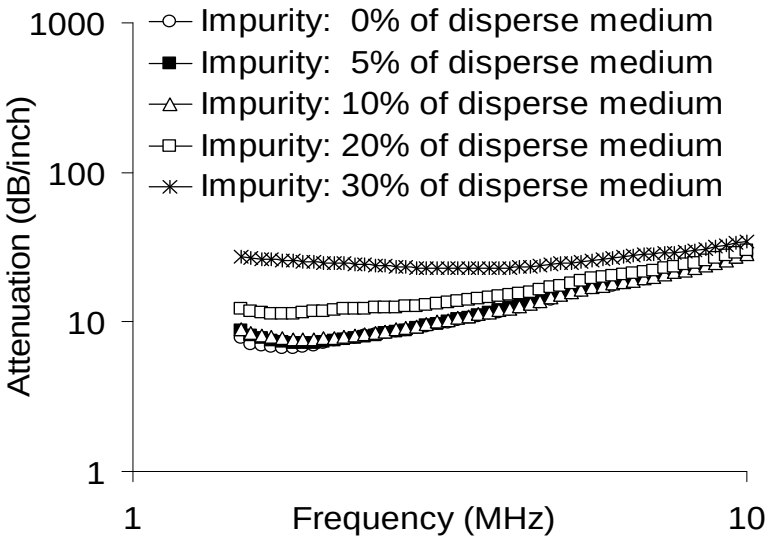

Fig. IV.7(a)

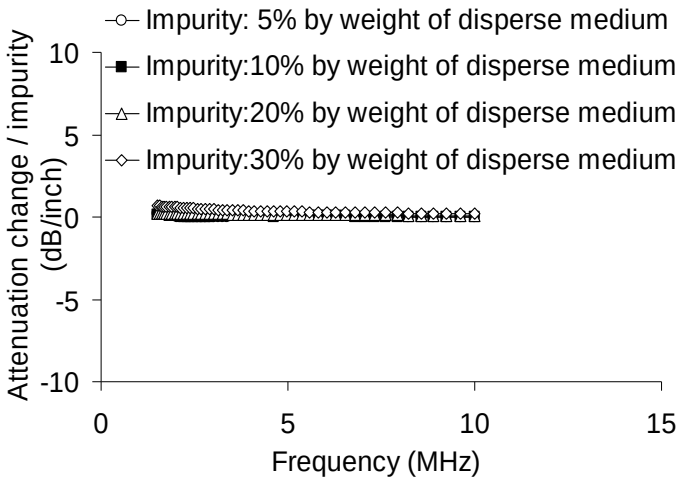

Fig. IV.7(b)

Fig. IV.7: (a) Effects of concentration of impurity of $NaNO_3$ on 10% (m/m) dispersion of $CaCO_3$. (b) Effects of concentration of impurity of $NaNO_3$ on 10% (m/m) dispersion of $CaCO_3$.

The method was applied to the entire series of the experiments in order to determine the conditions at which the effects of impurities can be predicted. Table IV.3 presents the results.

Table IV.3: Conditions in which effect of an impurity may be predicted			
Impurity	**5 % (m/m) dispersion of $CaCO_3$**	**10 % (m/m) dispersion of $CaCO_3$**	**20 % (m/m) dispersion of $CaCO_3$**
$MaCO_3$	Predictable effect	Predictable effect	Predictable effect
$NaNO_3$	Predictable effect	Predictable effect	Unpredictable effect
Sodium polyacrylate	Unpredictable effect	Unpredictable effect	Unpredictable effect

IV.8 Conclusions

The addition of an impurity into a dispersion may or may not change original particle (or aggregate) size of the disperse medium, depending on the conditions. With the help of acoustic attenuation spectroscopy, it is possible to predict the conditions (i - concentration of dispersion; ii - proportion of impurity) at which the particle (or aggregate) size of the disperse medium is not influenced by the addition of the impurity. In such cases, we can calculate the acoustic contribution of the impurity in the total acoustic attenuation spectrum of the dispersion. This contribution may be subtracted from the total attenuation spectrum of the dispersion in order to get more realistic information of the particle size of the disperse medium. The cases in which the size of the disperse medium seems to be influenced by the addition of certain quantities of impurities may be explained based on the existence of multiple scattering (a complex phenomenon that disturbs attenuation in acoustic measurement), interaction between particles of the disperse medium or interaction between particles of the impurity and those of the disperse medium. In such cases, it becomes more difficult to get exact particle size information of the disperse medium by using acoustic attenuation spectroscopy. In the study, higher quantities of impurities were considered in order to emphasize their effect on acoustic response. However, under usual conditions, when the proportion of an impurity is less than 20% of the weight of the disperse medium, it may be assumed that presence of the impurities in a dispersion may lead to predictable effects, except for the impurities (such as sodium polyacrylate) that may influence electrostatic and steric stabilization of the dispersions.

Pour conclure

Ce chapitre, dédié à la caractérisation de suspensions concentrées par spectroscopie acoustique, avait pour objet de préciser les conditions d'utilisation de cette technique de mesure pour des suspensions « réelles », c'est-à-dire telles qu'on peut les rencontrer dans des procédés de traitement industriels, et donc contenant des impuretés ou des additifs de différentes natures. L'étude a été menée sur des suspensions aqueuses de carbonate de calcium à différentes concentrations (entre 5 et 20 % massique), en présence de carbonate de magnésium (impureté insoluble), de nitrate de sodium (impureté soluble) ou de polyacrylate de sodium, qui est un additif soluble, couramment utilisé pour ses propriétés dispersantes. Pour ces trois additifs, des concentrations variables entre 5 et 30% (par rapport à la masse de $CaC0_3$) ont été considérées. Ces additifs ou impuretés sont généralement présents dans les suspensions de carbonate de calcium avec des concentrations nettement plus faibles que celles qui ont été considérées ici, mais nous voulions nous placer dans des conditions extrêmes pour lesquelles on pouvait s'attendre à ce que la présence des additifs modifie significativement le spectre d'atténuation acoustique et ceci afin de déterminer les limites d'utilisation de la technologie.

L'addition d'une impureté (le terme étant pris ici au sens large) dans une dispersion peut ou ne pas changer l'état original de la dispersion, c'est-à-dire la taille des particules ou des agrégats initialement présents. Nous avons vu qu'avec la spectroscopie acoustique il était possible de prédire les conditions, en termes de concentration en solide de la dispersion et de proportion en impureté, pour lesquelles la taille des particules ou des agrégats dans la suspension n'était pas influencée par l'ajout de l'impureté. Dans ces conditions, nous pouvons calculer la contribution de l'impureté sur la réponse acoustique globale de la dispersion. La contribution spécifique liée aux impuretés peut alors être soustraite du spectre d'atténuation total, ce qui permet d'avoir une information plus réaliste de la distribution de taille des particules du produit dispersé. Dans ces situations, l'effet de la présence d'impureté a été qualifié de prévisible.

Les cas où la taille du produit dispersé semble être influencée par l'addition de certaines quantités d'impuretés peuvent être expliqués par l'existence d'un phénomène de diffusion acoustique multiple ou de phénomènes d'interaction entre les particules de la dispersion (agrégation ou de-agrégation) ou entre les particules du milieu dispersé et les impuretés. L'effet de l'impureté sur la réponse acoustique, soit parce qu'elle agit sur le phénomène d'atténuation acoustique, soit parce qu'elle induit une modification de l'état de dispersion de la suspension, est alors qualifié d'imprévisible. Dans ces situations, il n'est pas aisé d'obtenir une information précise sur la distribution de taille du produit dispersé par spectroscopie acoustique. Toutefois, les situations où les impuretés ont un effet imprévisible ont été observées soit pour de très fortes concentrations en impuretés (supérieures à 20%), ce qui n'est souvent pas le cas dans des conditions usuelles, soit lorsque les « impuretés », comme le polyacrylate de sodium dans le cas traité, modifient l'état de dispersion des particules

suspension. Le polyacrylate de sodium est en effet connu pour ses propriétés dispersantes. Il s'adsorbe à la surface des particules de carbonate de calcium et induit une répulsion entre les particules par effet électrostérique. Mais là encore les concentrations utilisées en pratique ne sont généralement pas aussi élevées.

IV.9 References

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Effects of Concentration of Dispersions on Particle Sizing during Production of Fine Particles in Wet Grinding Process

As per requirements of the university, a preface in the beginning and concluding remarks at the end of the chapter have been given in French.

Préface en français

Les limitations de la spectroscopie acoustique pour l'analyse de dispersions concentrées, pouvant contenir des impuretés ou des additifs ayant été précisées dans le chapitre précédent, ce chapitre montre l'utilisation de cette technologie pour le suivi en ligne d'un procédé de broyage en voie humide. Nous avons rappelé dans le chapitre II que les broyeurs à billes agités constituaient une technologie particulièrement intéressante pour produire des suspensions concentrées de particules de taille submicronique. Plusieurs études ont été menées dans le passé mettant en exergue les effets sur le résultat du broyage (finesse, rendement) de différents paramètres opératoires ; entre autres : la forme, la taille, la nature et le taux de charge des billes de broyage, la vitesse de rotation de l'agitateur dans la chambre de broyage, le débit de circulation de la suspension à traiter, etc. L'analyse de la bibliographie sur ces aspects a également montré que la concentration en solide dans la suspension était un paramètre important mais son effet est difficile à appréhender car il dépend du matériau traité. Une autre difficulté pour analyser l'effet de la concentration en solide dans les procédés de broyage est que la plupart des techniques usuelles de caractérisation de la distribution de taille nécessitent une dilution des échantillons avant la mesure. Dans ce chapitre, nous considèrerons donc en tout premier lieu la spectroscopie acoustique pour analyser l'effet de la concentration en solide sur l'évolution temporelle de la distribution de taille du carbonate de calcium en suspension en ligne du procédé de broyage par microbilles.

Les analyses préliminaires, décrites au chapitre III, réalisées en mélangeant deux lots de carbonate de calcium de taille moyenne différente sont rapportées ici et développées. En effet, lors d'un procédé de réduction de taille, la distribution de taille du produit évolue fortement. Un état intermédiaire, entre le produit initial et le produit broyé, est constitué par le mélange de grosses particules, qui sont des particules initiales non encore fragmentées, et des particules fines, qui sont des fragments.

Les résultats des mesures de taille effectuées par spectroscopie acoustique en ligne du procédé en conditions concentrées sont comparés à des résultats d'analyses effectuées off-ligne après dilution par diffusion dynamique de la lumière.

V. Effects of Concentration of Dispersions on Particle Sizing during Production of Fine Particles in Wet Grinding Process

This article presented in this chapter has been accepted in the journal of Powder Technology.
Paper title: Effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process.

Abstract: The stirred media milling is a prospective technology for producing colloidal dispersions by means of wet grinding process. In past, many researchers have studied the effects of different operating parameters such as size, shape, nature and quantity of grinding medium, the speed of agitator in grinding chamber, and the feed rate of dispersions etc. in stirred media mills. However, it is still less known how particle sizing which generate valuable information of particle size of the product to interpret, control and optimize the grinding process, is influenced by concentration of the dispersion during stirred media milling where particles change their size from micron to colloidal range rapidly. One of the reasons of this lack had been our incapability in the past to study the particle size distribution of dispersions without dilution. The recent advent of acoustic attenuation spectroscopy is known to be capable of studying dispersions without dilution, under real process conditions and on line. The study employs acoustic attenuation spectroscopy to investigate the effects of concentration of dispersions of $CaCO_3$ on its particle sizing during size reduction process in a stirred media mill (LabStar manufactured by NETZSCH). The dispersions of $CaCO_3$ at 5%, 10%, 20% and 30 % (m/m) were studied about six hours under a selected set of operating conditions. Contrary to the existing knowledge obtained through other techniques of particle sizing that are based on principle of dilution, acoustic attenuation spectroscopy shows that, under certain grinding time at given operating conditions, increase in concentration of a dispersion results in better grinding results yielding smaller particles. The causes behind differences in results of acoustic attenuation spectroscopy and dynamic light scattering have been thoroughly investigated. We find certain limitations of acoustic attenuation spectroscopy in particle sizing. A typical phenomenon which causes misleading trends in particle sizing is multiple scattering in acoustic measurements. Multiple scattering, particularly, influences acoustic results when particles approach to fine size range during size reduction process.

Keywords: Acoustic attenuation spectroscopy, dispersions, fine particles, dynamic light scattering, stirred media mills, wet grinding.

V.1 Introduction

Many industries such as of paints, dyes, cosmetics, pharmaceuticals, ceramics and micro-electronics etc. employ colloidal dispersions in fabrication of many products. The demand of such industries for stable colloidal dispersions is on increase because use of fine particles may improve homogeneity, solubility, strength and reactivity etc. In general, there are two approaches for production of fine particles: (i) Bottom-up (in which fine particles may be produced by a reaction, condensation or aggregation of molecules etc.). (ii) Top-down (in which coarse particles are ground to produce fine particles). Wet grinding is often employed for production of fine and ultrafine particles suspended in a liquid. The stirred media milling is a prospective technology in domain of wet grinding because of many advantages such as relative low agglomeration tendency, low material losses, less possibility of oxidation, easy handling of toxic materials, elimination of need of employing a device for air cleaning, elimination of the problem of dust explosion and better heat transfer options etc. In past, many researchers have studied various aspects of wet grinding process. Today, it is known to a considerable extent how different operating parameters such as size, shape, nature and quantity of grinding medium, the speed of agitator in grinding chamber, and the feed rate of dispersions may affect size reduction process in stirred mills under certain conditions. However, it is still less known how particle sizing which generate valuable information of particle size of the product to interpret, control and optimize the grinding process, is influenced by the concentration of a dispersion during stirred media milling where particles enter from micron to colloidal size rapidly. One of the reasons of this lack had been our incapability in the past to study the particle size distribution of dispersions without dilution. The techniques of particle sizing based on principles of laser diffraction and dynamic light scattering etc., may measure the particle size of a dispersion but they require the sample to be diluted before measurement. The dilution step may result in destabilization of dispersion, formation or deformation of flocs and/or aggregates etc. All the techniques based on the dilution step have risk of not showing right information of particle size which is quite important in understanding, controlling, designing and optimizing the grinding processes.

Acoustic attenuation spectroscopy, which has appeared, relatively, in recent past, is considered a solution for such problems. Different reviews on the technique explain that it has advantages over many existing techniques because of wide range of particle sizing (10nm to 1000µm), because of being non-destructive, non-invasive and capable of measuring dispersions on line, at real process conditions and without dilution till a concentration of 50% (m/m) under certain conditions (Alba et al., 1999, McClements, 2000). The technique has been employed in many studies for different applications. For example, Richter et al. (2006) employ it for characterization of polydisperse particles in micrometer range, Stolojanu and Prakash (2001) consider it for characterization of slurry systems, Tourbin and Frances (2009) monitor aggregation process of dense colloidal silica suspensions with this technique. Takeda and Goetz (1998) and other researchers like Hibberd et al. (1999) use the

technique for characterization of flocculation in different applications. The applications of the technique in domain of crystallization may be consulted in the work of Hipp et al. (2000), Mougin et al. (2003) and Mingzhong et al. (2004) etc. However, sufficient work has not been performed yet in application of the technique in fine wet grinding processes which are typical in the sense: (i) the change in average particle size of the product is rapid in the grinding mill due to breakage of particles, (ii) the degree of poly dispersity changes with time in grinding process and (iii) the nature of interaction between particles is non-colloidal before grinding operation which changes to colloidal with increasing grinding time. This study is an attempt to explore such complexities. In particular, we investigate how different concentrations of a dispersion influence particle sizing during production of fine particles in wet grinding process carried out by means of a stirred media mill.

V.2 Fundamentals of the techniques of particle sizing

V.2.1 Acoustic attenuation spectroscopy

When a sound wave of certain frequency is passed through a particulate system, it interacts with the particles (transmission, reflection, absorption and scattering etc.) and as a result it undergoes attenuation (decrease in amplitude) that can be measured in terms of attenuation coefficient. It is defined as decrease in the amplitude of the sound wave per unit distance travelled and may be expressed as (McClements, 2000):

$$\alpha = -\frac{1}{x}\ln\frac{A_x}{A_0} \qquad \ldots\ldots\ldots\ldots\ldots (5.1)$$

Where A_0 is the initial amplitude of the sound wave (x=0) and A_x is the amplitude after it has travelled a distance x as illustrated in figure V.1.

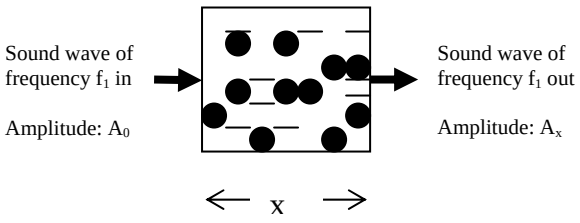

Fig. V.1: Passage of a sound wave through a dispersion.

If a band of sound waves of different frequencies is passed through a dispersion from a certain distance (x), the attenuations in each sound wave of certain frequency may be calculated using equation 5.1. An acoustic attenuation spectrum describes acoustic attenuation constants expressed as a function of frequencies of sound waves. There are two major steps in particle sizing by acoustic attenuation spectroscopy: (i) development of an acoustic attenuation spectrum and (ii) interpretation of

the resulting acoustic spectrum in terms of particle size distribution using an appropriate theory. A commercial acoustic attenuation spectrometer has appropriate arrangements for measurement of attenuation spectrum. Moreover, it has an appropriate software program to interpret acoustic attenuation spectrum in terms of particle size distribution based on some appropriate theory such as ECAH. This theory is based on differential waves equations that have been derived from fundamental laws of conservation of mass, energy, momentum, thermodynamic equations of state and stress-strain relations for isotropic elastic solids (or viscous fluids). The details of ECAH theory may be studied in papers of Epstein and Carhart (1953) and Allegra and Hawley (1972) who contributed to development of this theory.

V.2.2 Dynamic light scattering

Dynamic light scattering is also known as photon correlation spectroscopy. The basic principle of this technique is when particles are illuminated with laser; the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Smaller particles are pushed further by the solvent molecules and move more quickly. Analysis of these intensity fluctuations gives the velocity of the Brownian motion and thus the particle size using the Stokes-Einstein relationship. Dynamic Light Scattering measures hydrodynamic diameter which refers how a particle diffuses within a fluid. Hydrodynamic diameter is the diameter of a sphere that has the same translational diffusion coefficient as the particle being measured.

V.3 Materials

The aqueous dispersions of calcium carbonate were used in grinding, in this study. Availability of good literature on dispersing behavior of $CaCO_3$, its non- corrosive nature, low hazards and reasonable price make it, relatively, a good choice as a material of grinding in our study.

$CaCO_3$: It was procured through Merck KGaA Germany. It had purity > 99%, density = 2.656 g/cm^3 at 20˚C, thermal decomposition > 825˚C, specific surface area (BET) = 0.5 m^2 g^{-1} and hardness in the Mohs scale = 3. Its mean particle size (in dry form) was found to be 30 µm using technique of laser diffraction (Malvern Mastersizer). Its particle size distribution, as shown in figure V.2, explains that most of the particles had a size between a few microns and one hundred microns.

To study the shape of $CaCO_3$, Scanning Electron Microscopy (SEM) was employed. It was observed that the product is constituted by compact aggregates made of rhombohedral particles of about 30µm in size, as shown in figure V.2. A reasonable agreement was found in the results of both techniques.

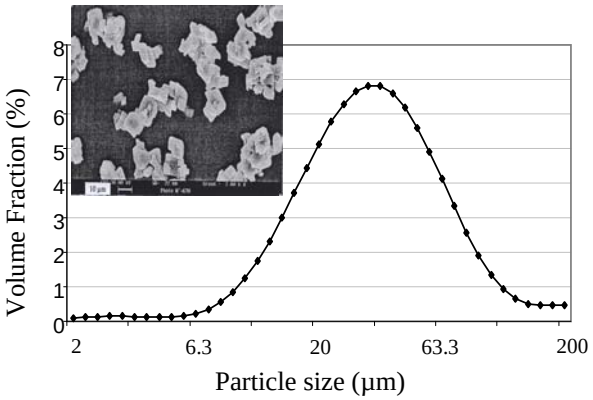

Fig. V.2: Particle size distribution and shape of $CaCO_3$ used.

Sodium polyacrylate: It was used as a dispersing agent. Foissy et al. have demonstrated its ability to disperse the particles of $CaCO_3$ in water (Foissy et al. 1982). It is based on anionic polyacrylate with a flexible chain able to form mono or bi coordinated complexes with the calcium ions of the solution. In ultrafine wet grinding for aqueous dispersions of $CaCO_3$, Garcia et al. (2004) have shown its suitability as a dispersing agent. It was procured through Sigma-Aldrich Co. It had density 0.55 g/cm^3 at 25 ˚C and average Mw ~5100 (determined by gel permeation chromatography (GPC)).

H_2O: Water served as dispersion medium in the dispersions employed in the study. Ultrapure water was produced by the equipment "Purelab Ultra" of VWS (UK) Ltd. Its density was found to be 0.9952 g/cm^3 at 25 ˚C where as its pH varied between 6.3-6.8 at 25 ˚C.

V.4 Experimental set up

Four dispersions, as mentioned in table V.1, were studied individually for about 6 hours in wet grinding process carried out in a stirred media mill that is commercially known as LabStar and manufactured by NETZSCH.

Table V.1: Compositions of dispersions used

	Disp. 1	Disp. 2	Disp. 3	Disp. 4
% Concentration (m/m)	5.000	10.000	20.000	30.000
% Concentration (v/v)	1.934	3.997	8.565	13.837
Water (g)	1700	1700	1700	1700
$CaCO_3$ (g)	89.47	188.89	425	728.57
Sodium Polyacrylate (g) (8% of mass of $CaCO_3$)	7.158	15.111	34.000	58.286

In each of the four cases, the dispersions (suspensions) were prepared in conical flask. Sodium polyacrylate was first dissolved in water with the help of a magnetic stirrer followed by addition of $CaCO_3$. All dispersions were agitated at 1100 r.p.m. for about 20 minutes at 25 ˚C before transferring them to stirrer tank for starting comminution. Figure V.3 shows the experimental set-up that provides a circuit mode comminution of the product. In general, in each of the four cases, the dispersion was pumped through the stirrer tank to the inlet of the grinding chamber of the stirred media mill (LabStar) with the help of flexible-tube pump. After experiencing a certain comminution in grinding chamber, the dispersion left through a steel (Cr-Ni-steel) separating cartridge (filter) that was installed at out let of the grinding chamber. The dispersion was recycled to the stirred tank after being passed through the acoustic attenuation spectrometer for online measurement of particle size in real environment (i.e. without need of dilution, on line and at process conditions).

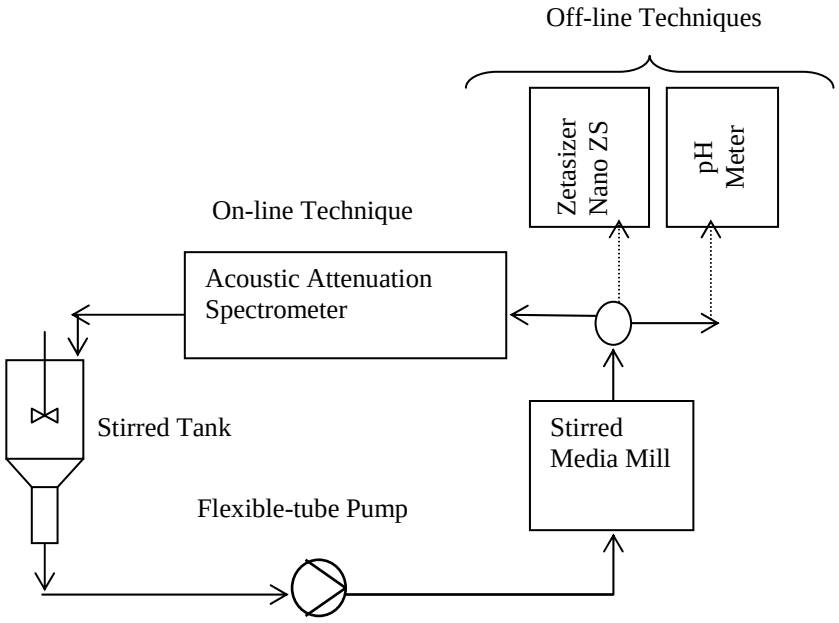

Fig. V.3: Experimental setup.

We had access to an acoustic attenuation spectrometer called Malvern Ultrasizer to measure the acoustic attenuation spectra of the dispersions and determining particle size distributions. The full details of the equipment are mentioned in US patent No. 5,121,629 3 (Alba et al., 1999). Table V.2 shows the set of physical properties (matrix) that was used in determination of particle size distributions using the software of the acoustic attenuation spectrometer.

Table V.2: Physical properties at 25˚C used in calculations for particle sizing	
$CaCO_3$:	
Density (g. cm $^{-3}$)	2.6560
Sound speed (cm.s^{-1})	5.5600x10^{5}
Thermal dilation (˚C^{-1})	2.2130x10^{-6}
Thermal conductivity (erg .cm^{-1}. s^{-1}. ˚C^{-1})	2.2594 x10^{5}
Heat capacity (erg. g^{-1}. ˚C^{-1})	8.3680 x10^{6}
Shear rigidity (dynes.cm^{-2})	3.0800 x10^{11}
Water:	
Density (g. cm $^{-3}$)	9.9524 x10^{-1}
Sound speed (cm.s^{-1})	1.4970 x10^{5}
Thermal dilation (˚C^{-1})	2.5677 x10^{-4}
Thermal conductivity (erg .cm^{-1}. s^{-1}. ˚C^{-1})	5.9525 x10^{4}
Heat capacity (erg. g^{-1}. ˚C^{-1})	4.1785 x10^{7}
Viscosity	9.0300 x10^{-3}

In particle size determination by Malvern Ultrasizer, “spectral quality” and “residual” are two important quality parameters that must be ≤5 for acceptable results. All acoustic measurements in the study meet quality criteria.

From the outlet of the grinding mill after certain intervals of time, the samples of the product were taken manually to analyze with pH meter and Zetasizer Nano ZS. The later is manufactured by Malvern Instruments, works on principle of dynamic light scattering and measures zeta potential and particle size distribution of dilute samples. A reasonable repeatability was found in all the measurements taken by Malvern Ultrasizer, Zetasizer Nano ZS and pH meter. In the grinding mill (LabStar), torque and number of revolutions were measured by a torque sensor that was installed at a stirrer shaft by the manufacturer of the mill. The problem of contamination of the product by the materials of the mill had been reduced in the grinding chamber by lining with Cr-Ni-stirred walls and equipping the agitator shaft with tungsten-carbide pegs. The core objective of the experiments was to study the influence of concentrations of dispersions (as mentioned in table V.1) on particle sizing of the product obtained after certain times under a set of fixed operating parameters as described in table V.3.

Table V.3: Set of fixed operating parameters	
Grinding media:	Zirconium oxide beads stabilized by yttrium
Size of grinding media:	300-500 µm
Density of grinding media:	3.7850 g/cm^{3}
Volume of grinding media:	415 ± 2 cm^{3}
Volume of grinding chamber:	670 cm^{3}
Flow rate of dispersion:	4.82 ± 0.1 cm^{3}/s
Grinding system:	Zeta
Speed of stirrer in grinding chamber:	1500 rpm
Speed of agitator in stirred tank:	600 rpm
Separating cartridge (filter):	100 µm
Temperature:	25˚C

The residence times in case of 5%, 10%, 20% and 30 % (m/m) aqueous dispersions of $CaCO_3$ were 52.3 minutes, 50.8 minutes, 47.6 minutes and 44.0 minutes respectively.

V.5 Results and discussion

V.5.1 General considerations in particle sizing

It has been discussed that particle sizing in fine wet grinding process is typical in the sense: (i) The change in average particle size of the product is rapid due to relatively fast breakage of particles. (ii) The degree of poly dispersity in product changes with grinding time. (iii) The nature of interaction between particles is non-colloidal before grinding process; this interaction becomes colloidal after a certain grinding time.

In our preliminary work (i.e. before experiments of stirred media milling), we have verified suitability of acoustic attenuation spectroscopy for measuring the changes discussed in (i) and (ii) by taking into consideration different dispersions prepared with different proportions of coarse $CaCO_3$ (30 µm) and relatively fine $CaCO_3$ (1.6µm), as mentioned in table V.4.

Table V.4: Aqueous dispersions of $CaCO_3$ mixed with different proportion of coarse and relatively fine particles.

Dispersion No.	H_2O Ca	CO_3 (30 µm)	$CaCO_3$ (1.6 µm)
g		g	g
(1)	700	200	0
(2)	700	0	5
(3)	700	0	25
(4)	700	0	50
(5)	700	0	100
(6)	700	0	150
(7)	700	200	5
(8)	700	200	25
(9)	700	200	50
(10)	700	200	100
(11)	700	200	150

Acoustic attenuation spectroscopy is capable of detecting the changes in dispersions due to increase in quantity of fine particles, and due to variation of proportion of relatively fine particles. Figures V.4 (a) and V.4 (b) demonstrate this respectively.

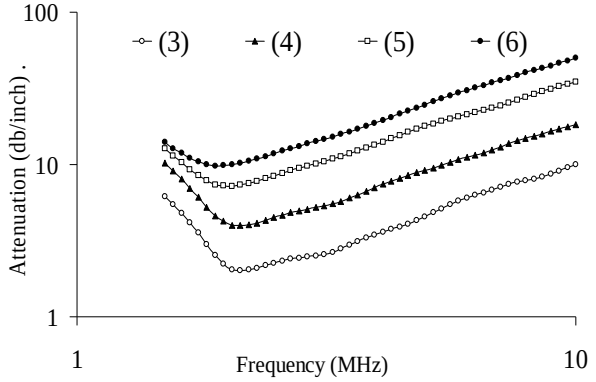

Fig. V.4 (a)

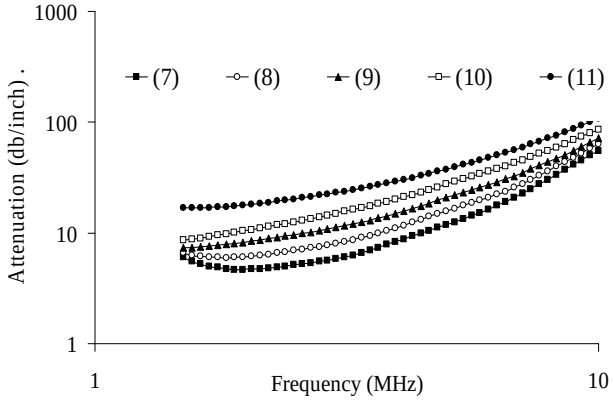

Fig. V.4 (b)

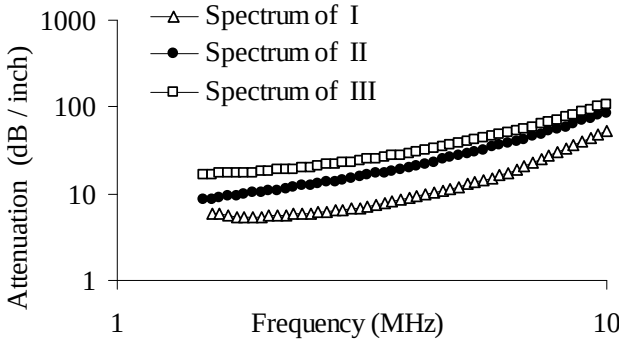

Fig. V.4 (c)

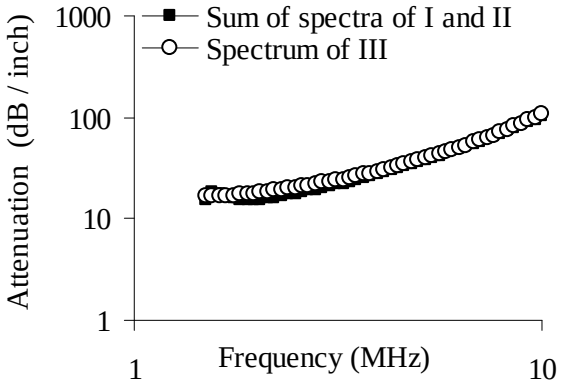

Fig. V.4 (d)

Fig. V.4: (a) Changes in acoustic spectra due to increase in quantity of relatively fine particles (b) Changes in acoustic spectra due to changes in proportion of relatively fine particles. (c) Acoustic spectra corresponding to different disperse media. (d) Comparison of acoustic attenuation spectra.

The results have been further verified. We describe the method of verification with the help of an example that focuses on dispersion nos. (1), (6) and (11) referred in table V.4. For these dispersions, acoustic attenuation spectra were determined with the help of acoustic attenuation spectrometer. Tourbin and Frances (2007) have given the expression for the attenuation spectrum of water as a function of frequency (*f*) as:

$$\alpha_w(f) = (0.0047 f^2 - 0.0083 f) \quad \ldots\ldots\ldots \quad (5.2)$$

From acoustic attenuation spectra of each dispersion, the acoustic contribution of water was subtracted in order to get the acoustic attenuation spectra merely due to particles present in the dispersions. Figure V.4 (c) represents resulting acoustic attenuation spectra corresponding to (I) 200 gram of

$CaCO_3$ (30 µm), (II) 150 gram of $CaCO_3$ (1.6 µm) and (III) a mixture of 200 gram of $CaCO_3$ (30 µm) and 150 gram of $CaCO_3$ (1.6 µm). If sum of the acoustic attenuation spectra of (I) and (II) is equal to acoustic attenuation spectrum of (III), then it may be considered that the technique is able to detect presence of both fine and coarse particles. Figure V.4 (d) compares the sum of acoustic attenuation spectra of (I) and (II) with acoustic attenuation spectrum of (III). The reasonable agreement in the results confirms the suitability of acoustic attenuation spectroscopy for measuring the changes discussed in (i) and (ii).

V.5.2 Effects of concentration of dispersions on particle sizing during wet grinding

V.5.2.1 Particle sizing by acoustic attenuation spectroscopy

It has been mentioned that grinding experiments were planned to study the effects of concentration of aqueous dispersions of $CaCO_3$ at varying proportions (i.e. 5%, 10%, 20%, 30 % (m/m)). The particle sizing of aqueous dispersion of $CaCO_3$ was carried out online, at real process conditions and without diluting the sample by means of acoustic attenuation spectroscopy. The results of average particle size of the dispersions obtained at different grinding times have been mentioned in figure V.5.

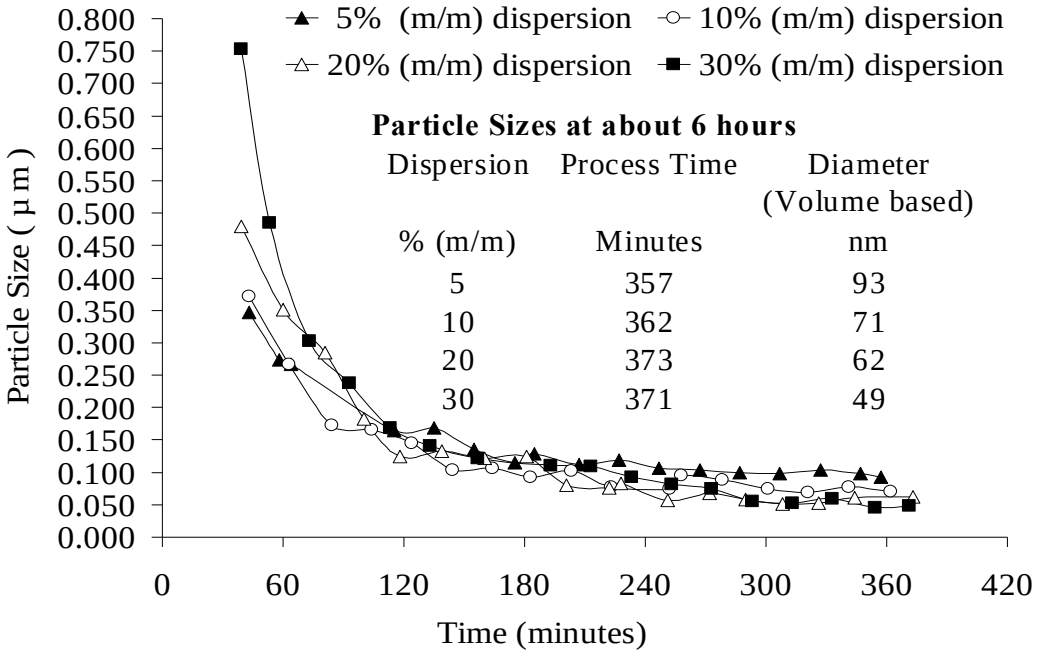

Fig. V.5: Particle sizes measured by acoustic attenuation spectroscopy during size reduction process in stirred media mill.

In beginning of the grinding process (i.e. first hour), the comparative study reveals that the higher is dilution of a dispersion, the smaller is its average particle size (i.e. use of dilute dispersion favors the process of size reduction). With time, when particles undergo further size reduction, a change in

tendency is observed. From second to sixth hour of grinding, it is evident that dispersion of 5 % (m/m) has bigger average particle size in comparison with all other dispersions. From second to third hour of grinding, the dispersion of 10 % (m/m) mostly shows the least average particle size as compared to all other dispersions. The change in trend becomes more evident from 3rd to 5th hours of grinding where dispersion of 20% (m/m) shows mostly least average particle size in comparisons to other dispersions. The sixth hour of grinding shows a completely inverse trend as compared to the trend observed in beginning of the grinding process (i.e. the higher is concentration of a dispersion, the smaller is its average particle size) or in other words, the use of concentrated dispersions favors the process of size reduction.

V.5.2.2 Particle sizing by dynamic light scattering

The technique of dynamic light scattering is different from acoustic attenuation spectroscopy in two major aspects: (i) It measures the particle size of dispersions in dilute state. (ii) The particle size measured by this technique is hydrodynamic and not volume-based as in acoustic attenuation spectroscopy. The figure V.6 demonstrates the results of average particle size of the dispersions obtained at different grinding times.

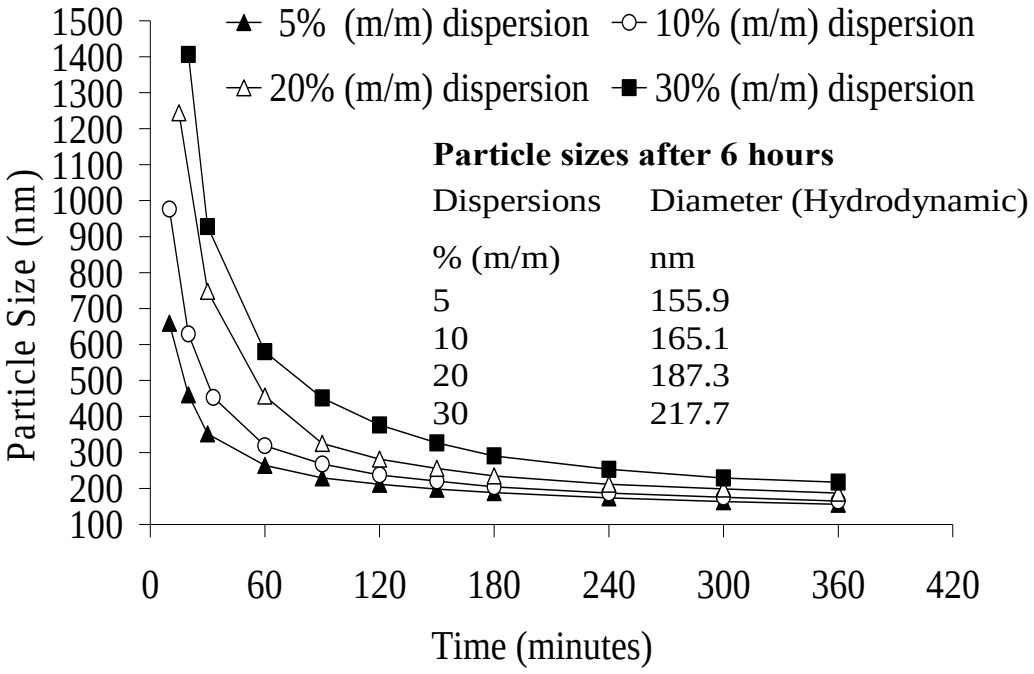

Fig. V.6: Particle sizes measured by dynamic light scattering during size reduction process in stirred media mill.

The results explain that size reduction process is favored by use of dilute concentrations. The trend remains un-changed throughout the grinding process.

V.5.3 Causes of different trends

Techniques of acoustic attenuation spectroscopy and dynamic light scattering generate different results in terms of numerical values and trends as shown in figure V.7. In absence of scientific explanation of such opposing trends, one may get misled during process of controlling, designing and optimizing the wet grinding process for production of fine particles. It is, therefore, important to investigate the roots of the problem that may lie in the process of particle sizing. The following hypotheses were developed in order to investigate the problem.

H1: Different trends are due to different types of diameters of particles measured by two different techniques of particle sizing.

H2: Different trends are due to dilution of samples, in case of particle sizing by dynamic light scattering, which changes the particle size generating misleading information.

H3: The two different trends are due to multiple scattering in acoustic measurements that generates misleading information.

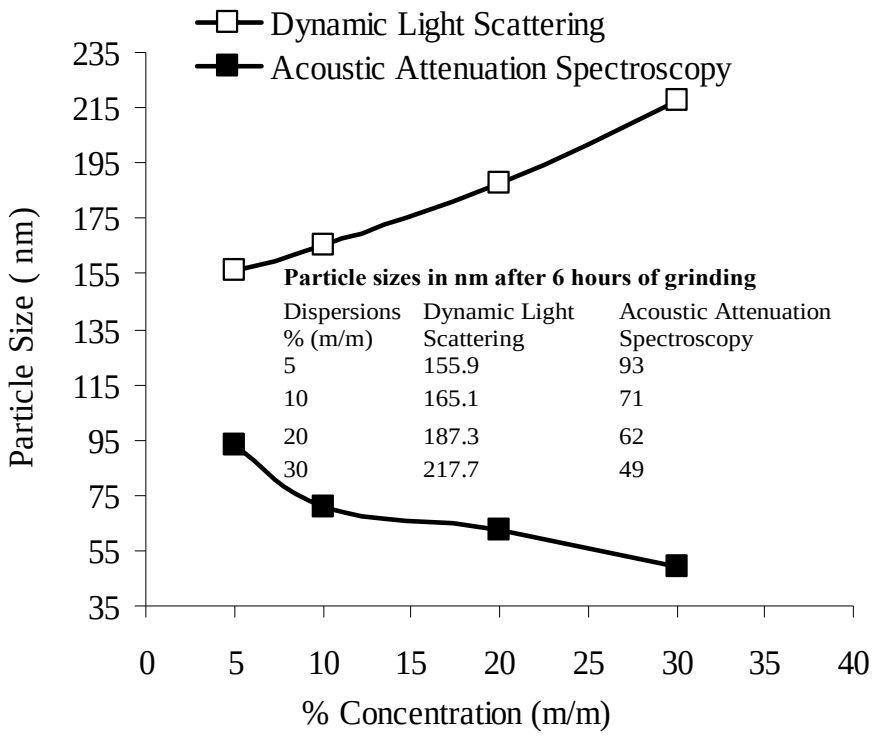

Fig. V.7: Particle sizes of the dispersions measured by two different techniques after about 6hrs of grinding.

V.5.3.1 Effects of different diameters on measurements

The diameter of particles measured by dynamic light scattering is hydrodynamic diameter. Based upon theory behind the technique (section V.2.2), hydrodynamic diameter may be regarded as the diameter

of the particle plus the thickness of the layer of ions surrounding the particle, at both ends of the diameter (Tourbin and Frances, 2007). Approximately, $D_H = D+2/k$ (where D_H = Hydrodynamic diameter, D = Diameter of particle and $1/k$= thickness of layers of ions around particle, known as Debye length) (Tourbin and Frances, 2007). The value of the thickness of the layer of ions (from both ends of diameters) may be subtracted from the hydrodynamic diameter in order to get diameter of the particle (D). The method proposed by Israelachivili for the calculation of Debye length was employed (Israelachvili, 1992). For the electrolytes at 25˚C involving monovalent cations and anions (such as sodium polyacrylate), the following equation may be used for calculation of Debye length (Israelachvili 1992):

$$\frac{1}{\kappa} = \frac{0.304}{\sqrt{[Electrolytes]}} \qquad \ldots\ldots\ldots\ldots (5.3)$$

Where $1/k$ = thickness in nanometers of layers of ions around particle known as Debye length, and [electrolytes] = concentration of the electrolyte in moles/litre. The magnitude of Debye length depends solely on the properties of the liquid and not on any property of the surface such as its potential or charge (Israelachvili, 1992). Table V.5 shows the results for diameter of particles (D) at 25˚C when particles of $CaCO_3$ (insoluble) are surrounded by sodium polyacrylate (electrolyte).

Table V.5: Debye length & diameter of particle (D) at 25˚C in different dispersions

Dispersion % (m/m)	Moles of Electrolyte	Concentration (moles/L)	$1/k$ (nm)	D_H (nm)	D (nm)
5	0.00140	0.000826	10.5800	155.9	134.7
10	0.00296	0.001743	7.2818	165.1	150.5
20	0.00667	0.003922	4.8545	187.3	177.6
30	0.01143	0.006723	3.7077	217.7	210.3

The results demonstrate that the trend (i.e. use of dilute dispersions favors size reduction) as observed in figure V.6 (in case of dynamic light scattering) remains the same even after subtracting the Debye lengths from the results of dynamic light scattering.

V.5.3.2 Effects of dilution

Acoustic attenuation spectroscopy and dynamic light scattering when employed for studying the effects of concentration on particle size in wet grinding, yielded two different trends disabling us reaching a conclusion. Particle sizing by dynamic light scattering requires the samples to be diluted before measuring the particle size. The step of dilution may change the particle size leading to

different trends. In order to investigate, all the dispersions (5%, 10%, 20%, 30% (m/m)) obtained after grinding experiments were diluted gradually. In principle, zeta potential may show the stability of a dispersion indicating any change in particle size or otherwise; but the option could not be employed as measurement of zeta potential itself with Zetasizer Nano ZS require dilute of the sample. Therefore to study the change in particle size with dilution, pH values and acoustic spectra were measured at each step of dilution. The maximum changes in pH values were found to be 0.31, 0.41, 0.77 and 0.88 respectively in process of dilution of the dispersions of 5%, 10%, 20%, 30% (m/m) as shown in the figure V.8.

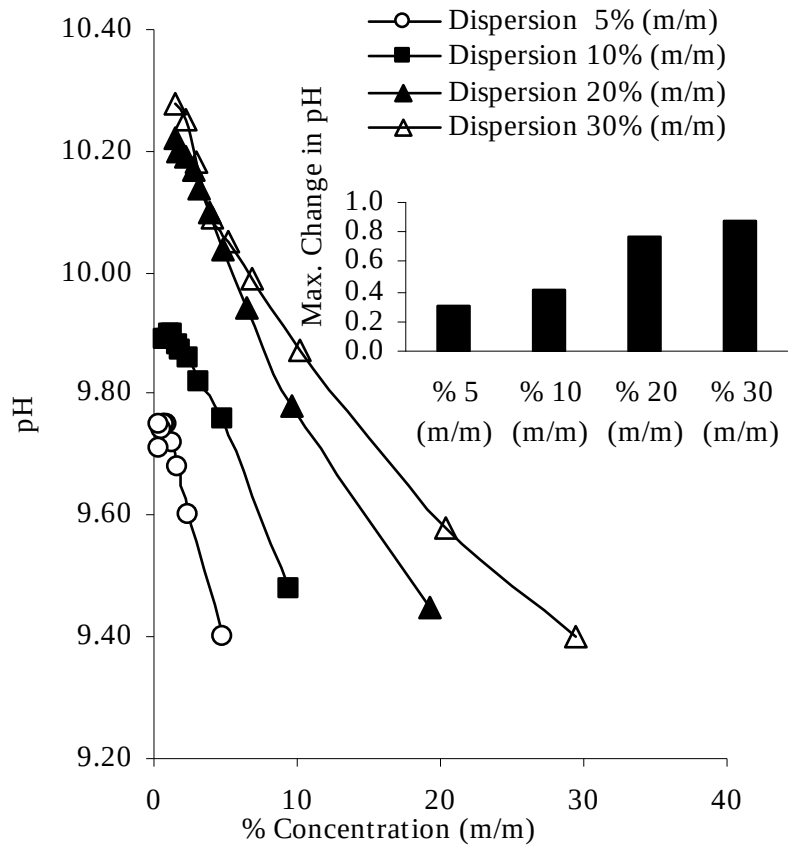

Fig. V.8: Changes in pH during dilution of dispersion after grinding.

The changes in values of pH are not considerably high. Zeta potential that can provide information about stability of dispersions was equally measured (by diluting the samples), in all dispersions after 6 hours of grinding, as shown in figure V.9. All the dispersions were found to be having values less than -26.6 mV indicating reasonable repulsive forces between the particles in the dispersions.

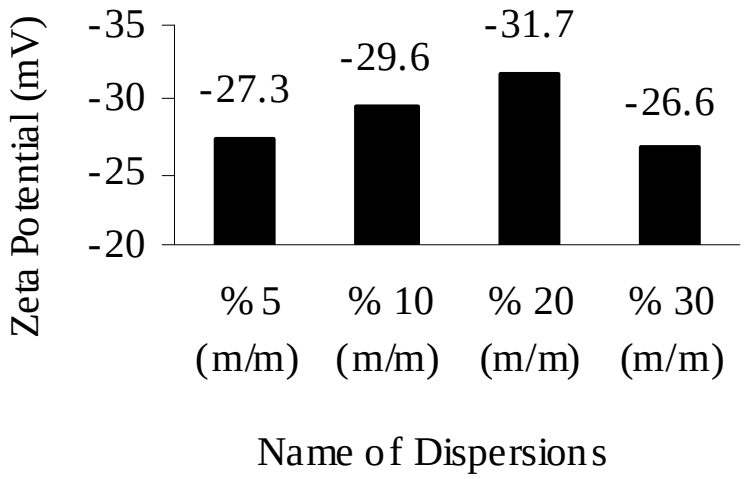

Fig. V.9: Zeta potential for the dispersions measured after 6 hours of grinding.

Change in Zeta potential depends upon change in pH, concentration or quantities of additives etc. Based on the results as shown in figure V.8 it can be considered that pH has not affected the zeta potential. It is difficult to study the effects of concentration change (dilution) on zeta potential using dynamic light scattering technique (Zetasizer Nano ZS). Acoustic attenuation spectroscopy, therefore, was employed at each step of dilution to understand how this technique explains the effects of dilution on stability and particle size. In general, we observed an ascending trend in particle size in dispersions of 20% (m/m) and 30% (m/m) whereas a descending trend in particle size in dispersions of 5% (m/m) and 10% (m/m) as shown in the figure V.10.

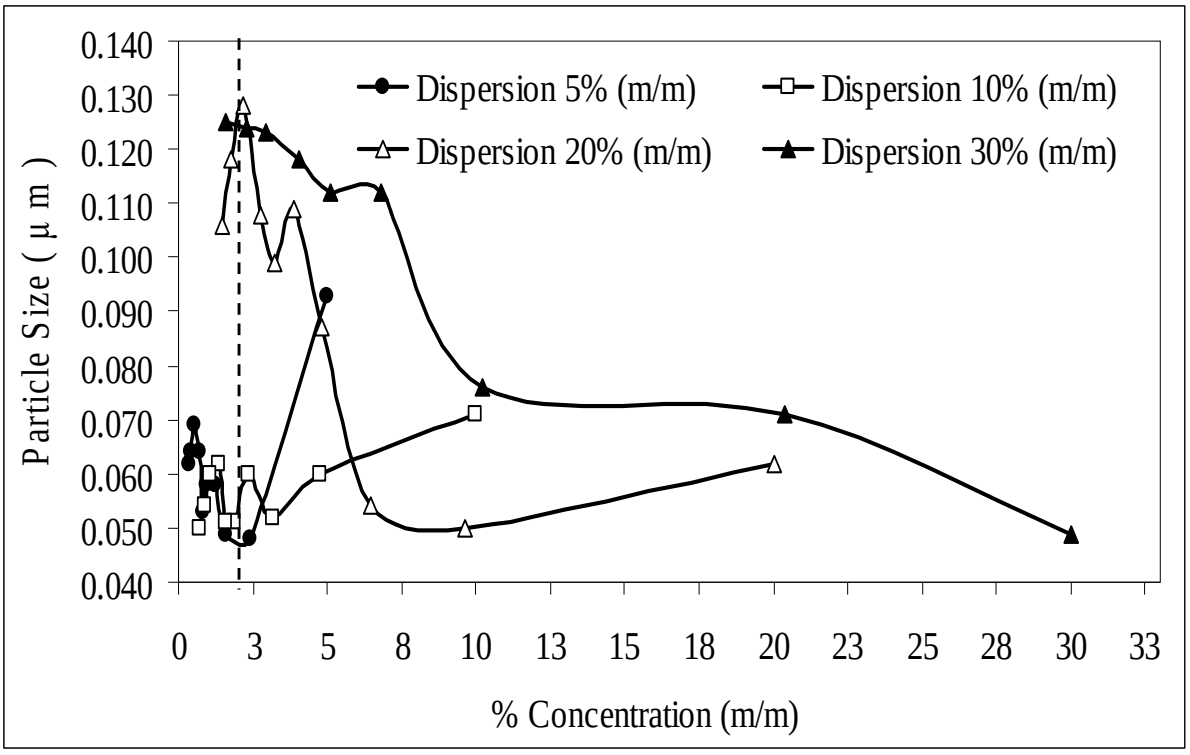

Fig. V.10: Particle sizes studied by acoustic attenuation spectroscopy on diluting the dispersions after grinding experiments.

Acoustic attenuation spectroscopy is unsuitable for analyzing very dilute dispersions (suspensions) particularly below 1% (m/m) (McClements, 2000). In our experiments, the limit of un-suitability seems to start from 2.6% (m/m) as mention by dotted line in figure V.10. A reason for ignoring the acoustic results during dilution process below the value of 2.6 % (m/m) is our pH study of the dispersions that indicated that pH values remained almost constant below that concentration. The figure V.11 compares the results of particle sizes obtained after 6 hours of grinding with the particle sizes of the same dispersions when each one was diluted to 2.6 % (m/m).

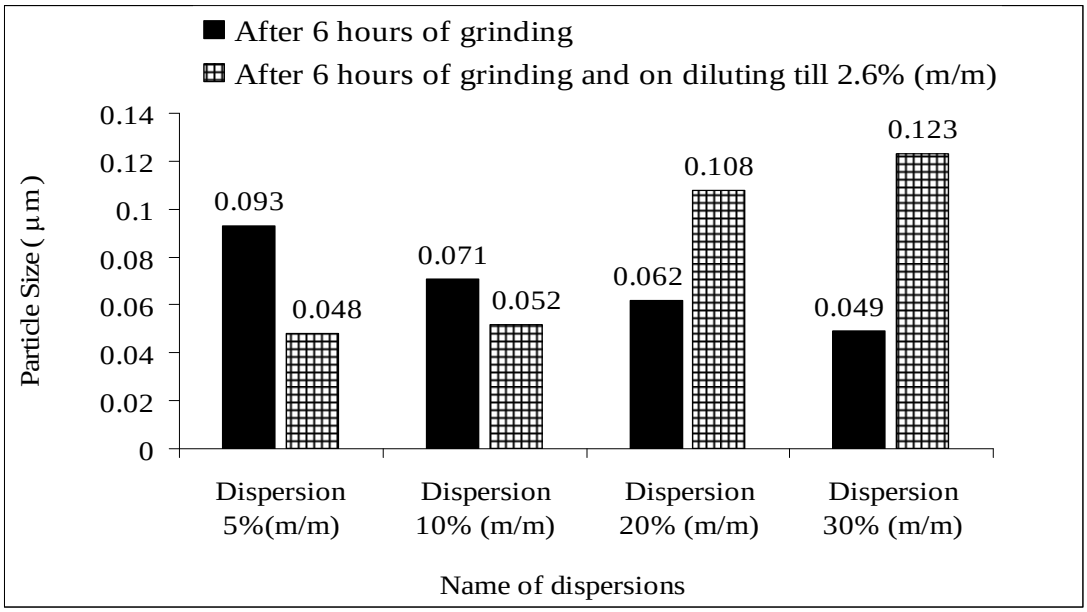

Fig. V.11: Comparative study of particle sizes by acoustic attenuation spectroscopy.

It is observed that trend is reversed. When this trend was compared with the trend in particle sizing by dynamic light scattering, both were found to be in accordance as shown in figure V.12.

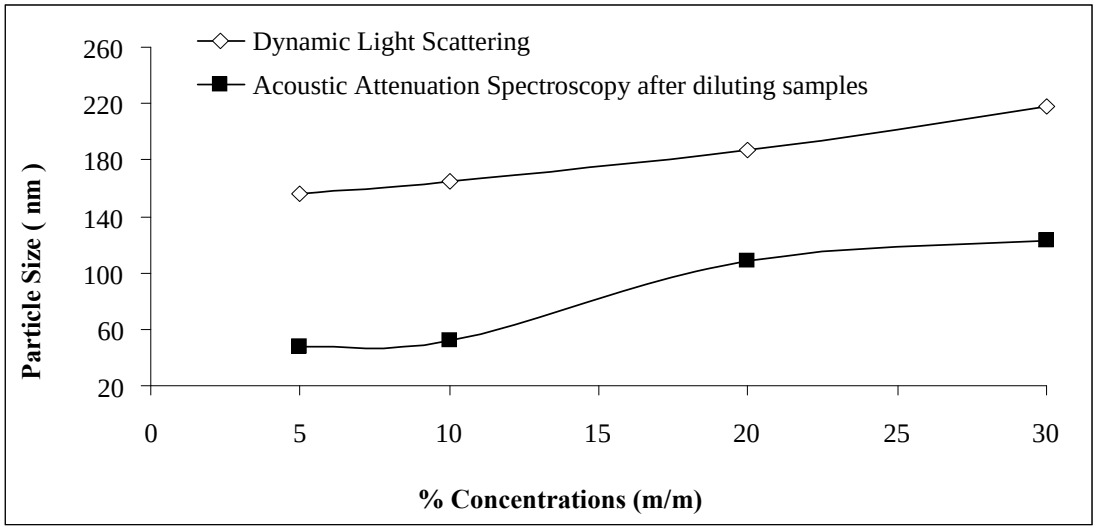

Fig. V.12: Comparative study of particle sizes by two different techniques after dilution.

V.5.3.3 Effects of multiple scattering

Multiple scattering is a phenomenon in which attenuated acoustic wave from one particle is scattered by other particles changing the acoustic signal and thus bringing to misleading results. Nonlinearity observed in acoustic curves (attenuation plotted as a function of concentration) may indicate the presence of multiple scattering (Tourbin and Frances, 2007; Hipp, 1999). The method adopted by Tourbin and Frances (2007) was followed to confirm the existence of multiple scattering. The method takes into consideration the excess of attenuation which may be described as (Tourbin and France, 2007):

$$\alpha_e(f) = \alpha_T - (1-\phi)(0.0047 f^2 - 0.0083 f) \quad \ldots\ldots\ldots \text{(5.4)}$$

Where $\alpha_e(f)$ = Excess attenuation (db/inch) at a certain frequency f, α_T = Total attenuation (db/inch) of the dispersion, ϕ = %Volume concentration of the dispersion, f= Frequency (MHz) of acoustic wave. A news series of experiments was performed to obtain data required in equation V.4. Each of the four dispersions (5%, 10%, 20%, 30% (m/m)), after grinding experiment were diluted to a certain volume concentration; ultrasound waves of different frequencies were passed through the dispersions to measure the excess and total attenuation in the sample. The dispersions were diluted further to several levels of volume concentrations and at each level of dilution the excess and total attenuations were measured. The same procedure was adopted in four cases of dispersions (5%, 10%, 20%, 30% (m/m)). Our investigation brings out that particles obtained after 6 hours of grinding process, in each case of the dispersions (5%, 10%, 20%, 30% (m/m), show multiple scattering. Figure V.13 demonstrates the excess of attenuation measured against concentration for the 20 % (m/m) dispersion as an example♣. Non linearity at different frequencies indicates presence of multiple scattering.

♣ *Supplementary results may be studied in appendix E at the end of this manuscript.*

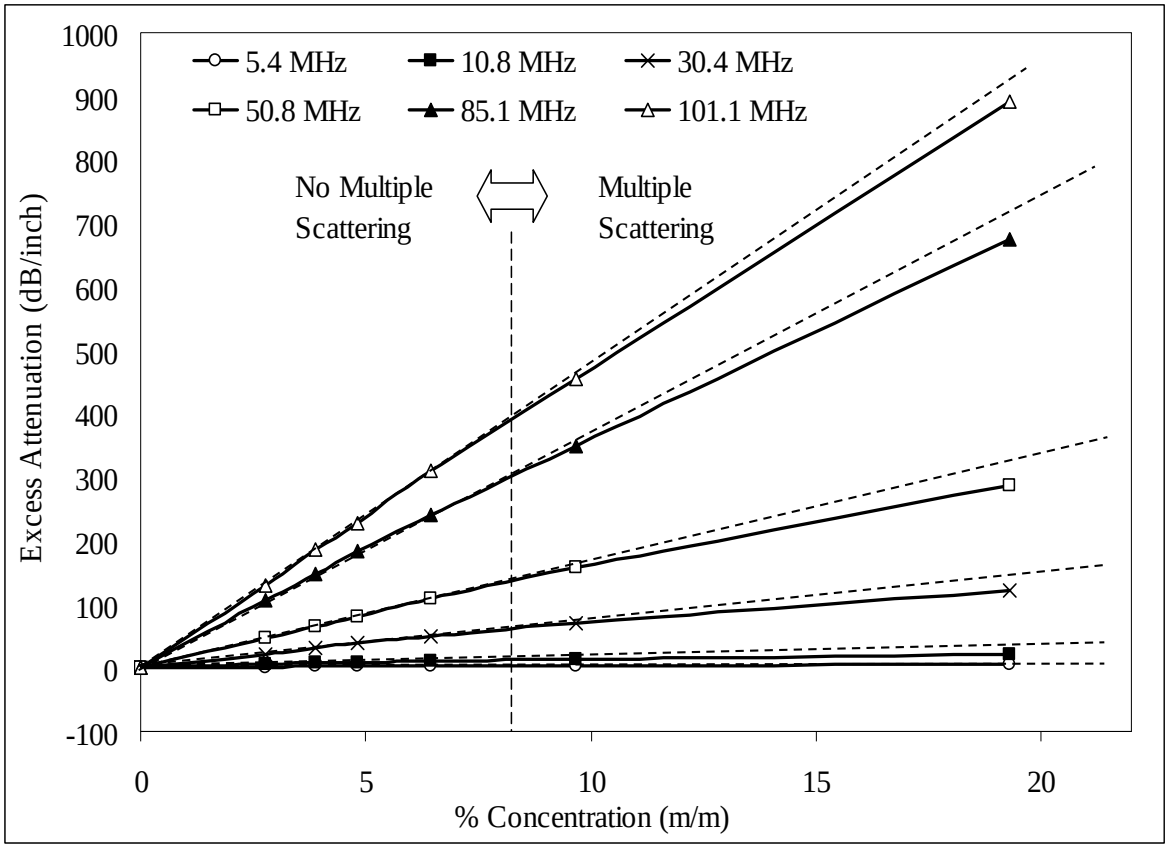

Fig. V.13: Multiple scattering in 20 % (m/m) dispersion.

V.6 Conclusions

The concentration of a dispersion plays an important role in particle sizing in size reduction process. This role emerges very distinctively when particles enter from micron to fine particle size range during stirred media milling. Acoustic attenuation spectroscopy, which is generally considered to be capable of measuring average particle size of the dispersions at different values of concentrations, shows certain limitations in stirred media milling. The technique explains that use of relatively concentrated dispersions may be favorable in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters. However, dynamic light scattering demonstrates that use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters. Our investigations brings out that particle sizing by acoustic attenuation spectroscopy cannot be considered valid at higher concentration of samples of dispersions during stirred media milling because of multiple scattering that influence the results. If concentration of the sample of dispersions is reduced considerably in particle sizing by means of acoustic attenuation spectroscopy in stirred media milling, then anomalies in the results may be

avoided. In such cases both the techniques shows reasonable agreement that use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters.

Pour conclure

Ce chapitre a été consacré à l'analyse du broyage de carbonate de calcium à l'aide d'un broyeur à billes agité de laboratoire. Plus particulièrement, nous avons cherché à analyser l'effet de la concentration en solide de la suspension traitée, qui est un paramètre essentiel dans les procédés de broyage en voie humide mais dont il difficile de prédire l'effet car il influence l'opération selon divers processus parfois contradictoires (influence sur la probabilité de capture des particules lors des impacts entre billes, modification du transport des particules dans les zones actives, influence sur le drainage du film lors du rapprochement des billes, effet sur les propriétés interparticulaires, …etc). La technique de spectroscopie acoustique a été utilisée pour suivre l'évolution de la distribution de taille des particules de carbonate de calcium en ligne du procédé lors d'un fonctionnement en re-circulation. Les mesures obtenues ainsi sur des suspensions concentrées ont été comparées à des analyses effectuées hors ligne par diffusion dynamique de la lumière après dilution des échantillons. Les résultats font apparaître des différences importantes, non seulement sur les données à proprement parlé (ce qui pourrait s'expliquer par le fait que les appareils concernés reposent sur des principes physiques totalement différents et ne permettent pas d'accéder aux mêmes grandeurs caractéristiques) mais également sur la tendance relevée en imposant lors du broyage des conditions de concentrations différentes. Ainsi, si les analyses sont effectuées par DLS, on observe que la taille des fragments est d'autant plus faible que l'opération de broyage a été réalisée à faible concentration et ceci quel que soit le temps de broyage considéré entre 0 et 6h d'opération. Au contraire, lorsque les analyses sont effectuées en ligne par spectroscope acoustique, on observe la même tendance au cours des deux premières heures de fonctionnement mais ensuite la tendance s'inverse ; la taille moyenne des fragments est d'autant plus faible que l'opération a été réalisée à forte concentration en solide.

Cet écart n'est évidemment pas acceptable car en situation de procédé industriel il engendrerait un mauvais contrôle du procédé ou une optimisation incorrecte des conditions de fonctionnement.

Plusieurs hypothèses ont été avancées pour expliquer les différences de résultats observées :

- des différences de tendance liées au fait que des dimensions différentes de particules sont déterminées par les deux techniques analytiques,
- des différences de tendance dues à la dilution des échantillons dans le cas des mesures effectuées par DLS qui pourrait modifier la taille des particules (processus d'agrégation ou de-agrégation)
- des différences dues au phénomène de diffusion acoustique multiple.

La DLS conduisant à une caractérisation du diamètre hydraulique des particules, il est possible par calcul de la longueur de Debye, d'estimer le diamètre des particules pour les différentes concentrations en solide considérées. Les diamètres calculés sont sensiblement différents, mais la tendance observée sur le résultat de l'opération de broyage en fonction de

la concentration reste la même. Aussi, même si la première hypothèse permettrait certainement d'expliquer les différences observées concernant les valeurs de la taille des particules données par les deux techniques de caractérisation, elle ne semble pas pouvoir justifier à elle seule le fait que l'on observe des tendances inverses.

Par ailleurs, des analyses de pH et de potentiel zeta sur les échantillons recueillis en fin d'opération de broyage n'ont pas révélé de différences vraiment significatives et suggèrent que les suspensions de carbonate de calcium restent stables au cours du temps de broyage, de même qu'après dilution.

En revanche, en analysant les échantillons de suspensions recueillis après les essais de broyage par spectroscopie acoustique et avec différentes dilutions, on a constaté une inversion dans la tendance relevée précédemment. Ainsi les deux techniques analytiques conduisent aux mêmes observations, à savoir que le processus de réduction de taille est favorisé lorsque la concentration en solide diminue.

Enfin, en considérant non pas l'atténuation acoustique de l'onde traversant le milieu dispersé mais l'excès d'atténuation en fonction de la concentration, il est possible d'évaluer l'écart au cas idéal où la contribution des particules est parfaitement additive en fonction de leur concentration (effet linéaire de la concentration). L'écart traduit alors le phénomène de diffusion multiple. On a observé que ce phénomène est présent pour toutes les concentrations considérées pour les échantillons obtenus après 6 heures de broyage. Il est donc possible que le phénomène de diffusion acoustique multiple soit responsable de l'inversion de tendance observée sur l'effet de la concentration en solide après deux heures de broyage, c'est à dire lorsque la taille moyenne des particules est de l'ordre de 150 nm (taille mesurée par spectroscopie acoustique). Ce résultat est conforme à ceux observés par Tourbin et Frances (2007) sur des suspensions concentrées de silice de taille nanométrique (100nm).

Aussi, si la technique de spectroscopie acoustique est intéressante pour suivre en ligne l'évolution de la distribution de taille lors d'un procédé de broyage en voie humide, elle s'avère moins adaptée lorsque on s'intéresse à la production de particules ultrafines (particules de taille inférieure à 200 nm environ).

V.7 References

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Effects of Particle Sizing and Operating Parameters on Product Quality in Wet Grinding Process

As per requirements of the university, a preface in the beginning and concluding remarks at the end of the chapter have been given in French.

Préface en français

Nous avons vu au chapitre V que la caractérisation de la distribution de taille des particules lors d'un procédé de broyage était une donnée essentielle et que la qualité du produit, en particulier sa finesse, pouvait dépendre de la technique de caractérisation utilisée. De manière plus générale, la qualité du produit broyé s'exprime au travers de différentes caractéristiques (la taille moyenne des particules après broyage, l'étalement de la distribution de taille, la stabilité de la suspension, la pureté du produit et d'autres propriétés, par exemple la couleur). La qualité du produit broyé est fonction du matériau (composition et pureté initiale, additifs utilisés, contamination éventuelle du produit lors du procédé), du broyeur (technologie de broyage utilisée), de la procédure de broyage (conditions de fonctionnement du broyeur), de la mesure (technique utilisée pour contrôler la qualité), de l'opérateur et du contrôle de l'opération. Ce chapitre constitue une extension des travaux réalisés dans les chapitres précédents, nous analysons les effets de trois paramètres importants : le matériau (dont la nature de l'additif utilisé et sa concentration), la procédure de broyage (en particulier la vitesse de rotation de l'agitateur) et la technique de mesure de la qualité. Concernant, ce dernier point, nous nous appuierons ici sur les essais décrits au chapitre précédent dans lequel nous avons comparé les résultats sur la mesure de taille obtenue par spectroscopie acoustique ou diffusion dynamique de la lumière.

VI. Effects of Particle Sizing and Operating Parameters on Product Quality in Wet Grinding Process

A paper based on this chapter has been orally presented in an international conference "The World Congress on Particle Technology" in Nuremberg Germany (26-29 April 2010).

VI.1 Introduction

Dispersions of fine and nanoparticles have applications in many fields such as paints, pigments, paper coatings, adhesives, catalysts, absorbent materials, fillers, printing inks, carbonless copying papers, emulsions, micro emulsions, ointments, ceramics, cement, fiber, reinforcement of plastics, dairy products, water proofing materials, cleansing agents and cosmetics amongst others. Fine and nano particles, due to small size and high surface area-to-volume ratios, exhibit physicochemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. They, generally, result in improvement of homogeneity, solubility, rheological properties, strength and reactivity etc. of the products formed with them. In wet grinding processes, stirred media milling is an interesting way of producing fine and nanoparticles. Stirred media which, as compared to tumbling and vibrating mills, are more suitable for producing high number of stress events per unit time and unit volume creating an appropriate stress intensity resulting in lower consumption of specific energy. In past, many studies have been carried out to understand production of fine and nanoparticles in stirred media mills by focusing on size of produced particles, mechanisms, different aspects of energies, nature of grinding materials and mediums, design and operating parameters etc. However, there is still lack of knowledge to understand how quality of final ground product is influenced in stirred media milling. This study is an attempt to understand how different operating parameters affect quality of final ground product. In particular, the effects of materials, methods and measurements on quality of final ground have been discussed in this study.

VI.2 Theoretical background

VI.2.1 Quality

Quality is an intangible concept because it is perceived individually. It is widely accepted that quality has both an objective and subjective dimension (Olsen et al., 2008). Olsen et al. (2008), Jover and

Montes (2004), Bremner (2000) amongst others argue that the perception of quality is shaped by both individual and contextual factors. In the literature, different perspectives to look at the quality have been discussed. Some important perspectives are summarized below:

Product oriented quality: This is mainly based upon product's characteristics.

Process oriented quality: This is based upon characteristics and principles of the production process. e.g., supply chain, policies, legal aspects, ethical standards of production etc.

User-oriented quality: This is based upon a user's subjective quality perceptions that may be influenced by quality factors of a more contextual nature. For example, the purchase situation and price etc.

VI.2.2 Product quality

VI.2.2.1 Inherent characteristics of a product

ISO 9000:2005 standard defines the term of quality as "A degree to which a set of inherent characteristics fulfils requirements". Based on this definition, the quantification of inherent characteristics of a product and thereafter its comparison with a certain set of requirements may provide an insight into quality of the product. In general, the inherent characteristics differ from one product to others. The focus of this study is on production of dispersions of fine and nanoparticles by means of stirred media milling. In this case, the set of inherent characteristics of the products may be constituted with:

- Average particle size of the product
- Range of particle sizes distribution of the product
- Stability of the product
- Purity of the product
- Physical appearance of the product (e.g. color, odor etc.)

VI.2.2.2 Product requirements

Inherent characteristics of a produced ground product may be measured against a given set of operating parameters of the mill. These inherent characteristics may be compared to selected product requirements (specifications) to comment on quality of the product at certain operating conditions. However, selecting a specific set of product requirements (specifications) may limit the application of the generated understanding and knowledge. This approach is not quite interesting in studying a grinding process. Another, interesting way is to consider many progressive sets of product requirements and look at the quality of the product at a certain set of operating parameters with reference to different sets of product requirements. Different set of product requirements may be regarded as different product grades. This approach, on one hand, will helpful in categorizing the

operating parameters that lead to a certain product grade and on the other hand will be helpful in generalizing the understanding and knowledge obtained through this study.

VI.2.3 Operating parameters

Ishikawa (1990) and later on others pointed out six important parameters (i.e. material, machine, method, measurement, manpower and management) that may influence quality in production of a product. In this study, we analyze the effects of three important operating parameters: (i) materials (ii) method (details of the process of wet grinding) (iii) measurement (especially of particle size) on product quality. The effects of machine (use of different grinding mills), manpower and management are out of the scope of this study.

VI.3 Materials

The composition and concentration of the grinding material may affect product quality in grinding process. This study focuses on grinding of aqueous dispersions of $CaCO_3$. Table VI.1 demonstrates different compositions and concentrations of aqueous dispersions of $CaCO_3$ that have been analyzed for understanding the effects on product quality.

Table VI.1: Compositions of materials (dispersions) employed in grinding experiments

Composition No.	Concentrations of aqueous dispersions of $CaCO_3$ (% m/m), (Cs)	Dispersants	% age of dispersant of the weight of $CaCO_3$
1	20	Targon-1128	2
2	20	Targon-1128	8
3	20	Agnique PG 8107-G	2
4	20	Agnique PG 8107-G	8
5	20	Sodium polyacrylate	2
6	20	Sodium polyacrylate	8
7	5	Sodium polyacrylate	8
8	10	Sodium polyacrylate	8
9	30	Sodium polyacrylate	8

$CaCO_3$: It was procured through Merck KGaA Germany. It had purity > 99%, density = 2656 kg m^{-3} at 20˚C, thermal decomposition > 825˚C, specific surface area (BET) = 0.5 m^2 g^{-1} and hardness in the Mohs scale = 3. Its mean particle size (in dry form) was found to be 30 µm using technique of laser diffraction (Malvern Mastersizer). To study the shape of $CaCO_3$, Scanning Electron Microscopy (SEM) was employed. It was observed that the product is constituted by compact aggregates made of rhombohedral particles of about 30µm in size.

Dispersing Agents: Three different dispersing agents were tested for dispersing the particles of $CaCO_3$ in water during grinding experiments.

(i)- AGNIQUE PG 8107-G, was obtained from Cognis GmbH Germany. It was based upon C8-10 alkyl polyglycoside. It had degree of polymerization 1.7, density 1.15-1.17 g/ml at 25 ˚C, water contents 28-32 % and pH 6-9.

(ii)- Sodium polyacrylate was procured through Sigma-Aldrich Co. It had density 0.55 g/ml at 25 ˚C and average M_w ~5100 (determined by gel permeation chromatography (GPC)). It was found to be highly soluble in water.

(iii)- Targon-1128, was obtained from BK Giulini Germany. It was based upon ammonium polycarboxylate. It had density 1.04-1.26 g/ml, pH 6.5-8.1 and water contents 61.9-66.1%.

H_2O: Water served as dispersion medium in the dispersions employed in this study. Ultrapure water was produced by the equipment "Purelab Ultra" of VWS (UK) Ltd. Its density was found to be 0.9952 g/cm^3 at 25 ˚C whereas its pH varied between 6.3-6.8 at 25 ˚C.

VI.4 Methods

LabStar manufactured by NETZSCH was employed as stirred media mill in this study for carrying out a circuit mode comminution of different material composition listed in table VI.1. The effects of two sets of operating conditions have been considered in this study. Table VI.1 provides their details.

Table VI.2: Operating conditions in stirred media milling

Set 1:	
Grinding media:	Zirconium oxide beads stabilized by yttrium
Size of grinding media:	300-500 µm
Density of grinding media:	3.7850 g/cm^3
Volume of grinding media:	415 ± 2 cm^3
Volume of grinding chamber:	670 cm3
Flow rate of dispersion:	4.82 ± 0.1 cm^3/s
Grinding system:	Zeta
Speed of agitator in stirred tank:	600 rpm
Separating cartridge (filter):	100 µm
Temperature:	25˚C
Speed of stirrer in grinding chamber:	1500 rpm
Set 2:	
Grinding media:	Zirconium oxide beads stabilized by yttrium
Size of grinding media:	300-500 µm
Density of grinding media:	3.7850 g/cm^3
Volume of grinding media:	415 ± 2 cm^3
Volume of grinding chamber:	670 cm3
Flow rate of dispersion:	4.82 ± 0.1 cm^3/s
Grinding system:	Zeta
Speed of agitator in stirred tank:	600 rpm
Separating cartridge (filter):	100 µm
Temperature:	25˚C
Speed of stirrer in grinding chamber:	2250 rpm

In each case, a dispersion was prepared by adding the respective quantity of the dispersant in water followed by continuous agitation with a magnetic stirrer. The respective quantity of $CaCO_3$ was added

thereafter. The system was kept agitated with the magnetic stirrer till homogeneity of the dispersion. The initial pH of the dispersion was maintained at 10.1 ± 0.5 using aqueous solutions of NaOH and HCl.

VI.5 Measurements

The conventional properties such as pH, temperature, density, energy etc. can be measured with a reasonable certainty in a grinding process. It is therefore, their effects on product quality have not been a matter of discussion in this study. The matter of measurement of particle size of a dispersion that is quite important in a grinding process has been taken into account in this study. The particle sizing generates valuable information of particle size of the product that is inevitable to interpret, control and optimize the grinding process. The particle sizing in production of fine and nanoparticles is typical from particle sizing in other processes in the senses: (i) the change in average particle size of the product is rapid due to relatively fast breakage of particles, (ii) the degree of poly dispersity in product changes with grinding time and (iii) the nature of interaction between particles is non-colloidal before grinding process; this interaction becomes colloidal after a certain grinding time. Techniques of acoustic attenuation spectroscopy and dynamic light scattering have been considered in this study for particle sizing during wet grinding process. The fundamentals of the techniques are described briefly.

VI.5.1 Acoustic attenuation spectroscopy

When a sound wave of certain frequency is passed through a particulate system, it interacts with the particles (transmission, reflection, absorption and scattering etc.) and as a result it undergoes attenuation (decrease in amplitude) that can be measured in terms of attenuation coefficient. It is defined as decrease in the amplitude of the sound wave per unit distance travelled and may be expressed as (McClements, 2000):

$$\alpha = -\frac{1}{x}\ln\frac{A_x}{A_0} \qquad \ldots\ldots\ldots\ldots\ldots (6.1)$$

Where A_0 is the initial amplitude of the sound wave (x=0) and A_x is the amplitude after it has travelled a distance x as illustrated in figure VI.1.

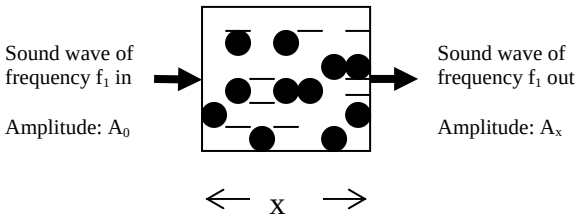

Fig. VI.1: Passage of a sound wave through a dispersion.

If a band of sound waves of different frequencies is passed through a dispersion from a certain distance (x), the attenuations in each sound wave of certain frequency may be calculated using equation 1. An acoustic attenuation spectrum describes acoustic attenuation constants expressed as a function of frequencies of sound waves. There are two major steps in particle sizing by acoustic attenuation spectroscopy: (i) Development of an acoustic attenuation spectrum. (ii) Interpretation of the resulting acoustic spectrum in terms of particle size distribution using an appropriate theory. A commercial acoustic attenuation spectrometer has appropriate arrangements for measurement of attenuation spectrum. Moreover, it has an appropriate software program to interpret acoustic attenuation spectrum in terms of particle size distribution based on some appropriate theory such as ECAH. This theory is based on differential waves equations that have been derived from fundamental laws of conservation of mass, energy, momentum, thermodynamic equations of state and stress-strain relations for isotropic elastic solids (or viscous fluids). The details of ECAH theory may be studied in papers of Epstein and Carhart (1953) and Allegra and Hawley (1972) who contributed to development of this theory.

VI.5.2 Dynamic light scattering

Dynamic light scattering is also known as photon correlation spectroscopy. The basic principle of this technique is when particles are illuminated with laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Smaller particles are pushed further by the solvent molecules and move more quickly. Analysis of these intensity fluctuations gives the velocity of the Brownian motion and thus the particle size using the Stokes-Einstein relationship. Dynamic Light Scattering measures a hydrodynamic diameter which refers to how a particle diffuses within a fluid. The Hydrodynamic diameter is the diameter of a sphere that has the same translational diffusion coefficient as the particle being measured.

VI.6 Equipments

VI.6.1 LabStar

A lab scale stirred media mill called LabStar, manufactured by NETZSCH, was used in the study. Control panel, grinding unit, supporting unit, peristaltic pump, conical shaped stirred tank, cooling device and computer system are main parts of the mill.

The function of the control panel is to control the speed of agitator, speed of pump and speed of mixer. The on-off switches and display screens for speed of agitator, speed of pump, power input for agitator are also part of control panel. Grinding unit is made of stainless steel and its volume is approximately 670 cm^3. The grinding unit consists in a pin shaped stirred for creating grinding impact in the grinding chamber. In a grinding experiment, the product in introduced in the conical shaped stirred tank that is mounted with an agitator to ensure homogeneity of the dispersion. The dispersion through the conical

shaped stirred tank is send to grinding unit with the help of peristaltic pump. In grinding unit, the comminution takes place. After experiencing a certain comminution in grinding chamber, the dispersion leaves through a steel (Cr-Ni-steel) separating cartridge (filter) that is installed at out let of the grinding chamber. The problem of contamination of the product by the materials of the mill has been attempted to reduce in the grinding unit by lining with Cr-Ni-stirred walls and equipping the agitator shaft with tungsten-carbide pegs. Supporting unit comprises of devices such as motor for rotating agitator (stirrer) in grinding chamber, pressure reducing valve, pressure switches, cooling pipes, security valves and sealing liquid for supporting grinding process. The cooling device with the help of circulating tubes around the grinding chamber removes the heat generated in grinding process. Computer system with LabStar is a stand alone computer that controls various functions of LabStar with the help of LabDot software.

VI.6.2 Ultrasizer

Ultrasizer (manufactured by Malvern Instruments Ltd.) that is based upon acoustic attenuation spectroscopy was used for particle sizing in this study. Malvern Ultrasizer produces a log-normal particle size distribution that is volume based i.e. frequency of each size class in the distribution would give a volume fraction of the total particulate volume within the sample.

VI.6.3 Zetasizer nano ZS

Zetasizer nano ZS (manufactured by Malvern Instruments Ltd.) that is based upon dynamic light scattering, was used in the study for measuring particle size and zeta potential of the dispersions. The equipment can measure the particle size of the dilute samples in the range of 0.6nm - 6µm. Zetasizer nano ZS produces a log-normal particle size distribution that is based upon intensity of scattered light. The measured equivalent diameter of the particles is often termed as hydrodynamic diameter.

VI.7 Results and discussions

VI.7.1 Effects of materials on product characteristics

This section analyzes how different compositions of the materials affect the product characteristics, when the materials are ground under the same operating conditions of the mill. The effects of nine different compositions of the dispersions, as mentioned in table VI.1, have been investigated in this study. The experimental results have been divided into four cases.

VI.7.1.1 Case A

In case A, the results of the effects of three different compositions (1, 3 and 5) of the materials (dispersions) on characteristics of the product have been discussed. The wet grinding of all three dispersions was carried out under the same operating condition of the mill (set 1, table VI.2).

The compositions of three dispersions differed in terms of type of added dispersants. The dispersants Targon-1128, Agnique PG 8107-G and sodium polyacrylate were employed in the compositions 1, 3 and 5 respectively. However, the concentrations of the dispersions and the proportion of added dispersants in all the dispersions was the same (i.e. 2% of the weight of the $CaCO_3$).

The figure VI.2 and VI.3 shows the progression of grinding processes in above mentioned dispersions along time and specific energy.

It is evident that the dispersions of composition 1and composition 5 undergo, relatively, an efficient size reduction process. The size reduction process, in case of the dispersion of composition 3, is the most in-efficient. In order to understand the reasons of the differences in the above three grinding processes, the values of zeta potential of the dispersions were studied at different intervals of time during grinding processes. The results have been presented in figure VI.4.

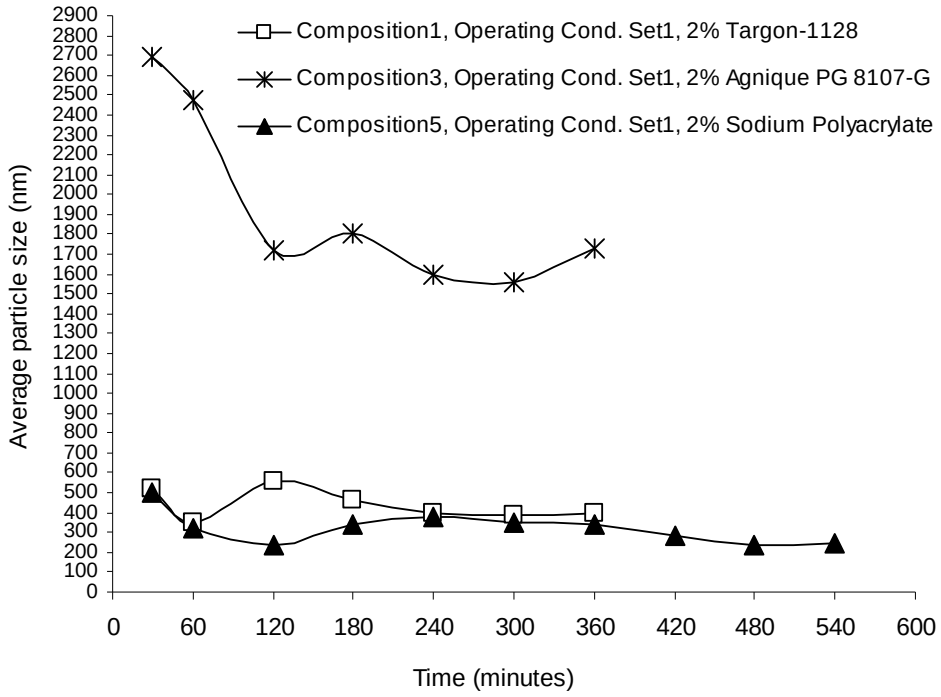

Fig. VI.2: Progression of size reduction process against time in the compositions 1, 3 and 5 at set 1 of operating conditions.

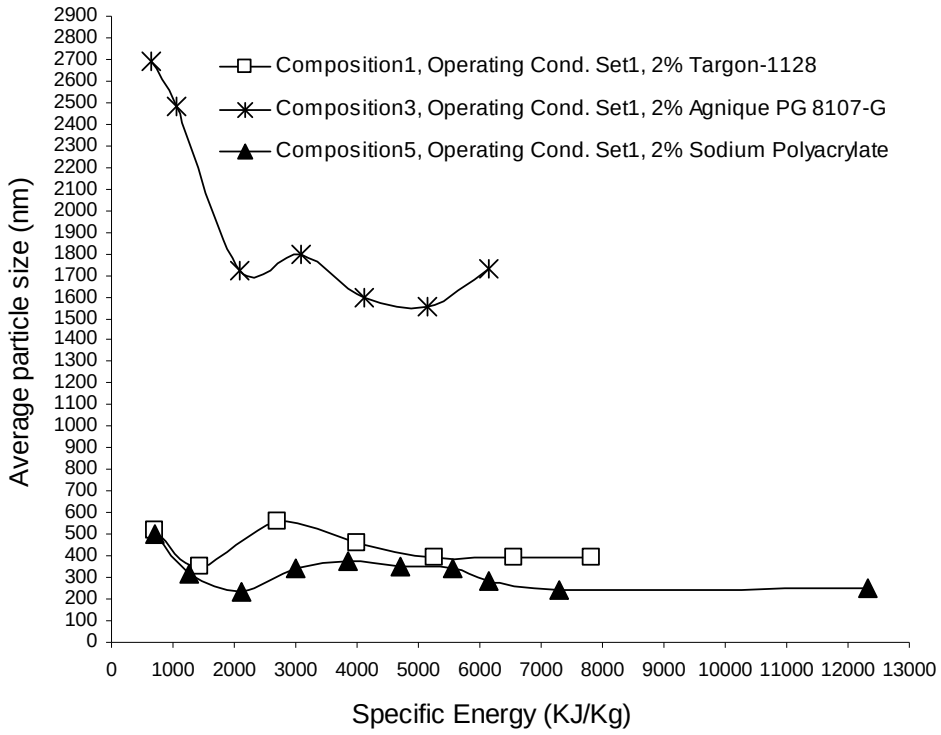

Fig. VI.3: Progression of size reduction process against specific energy in the compositions 1, 3 and 5 at set 1 of operating conditions.

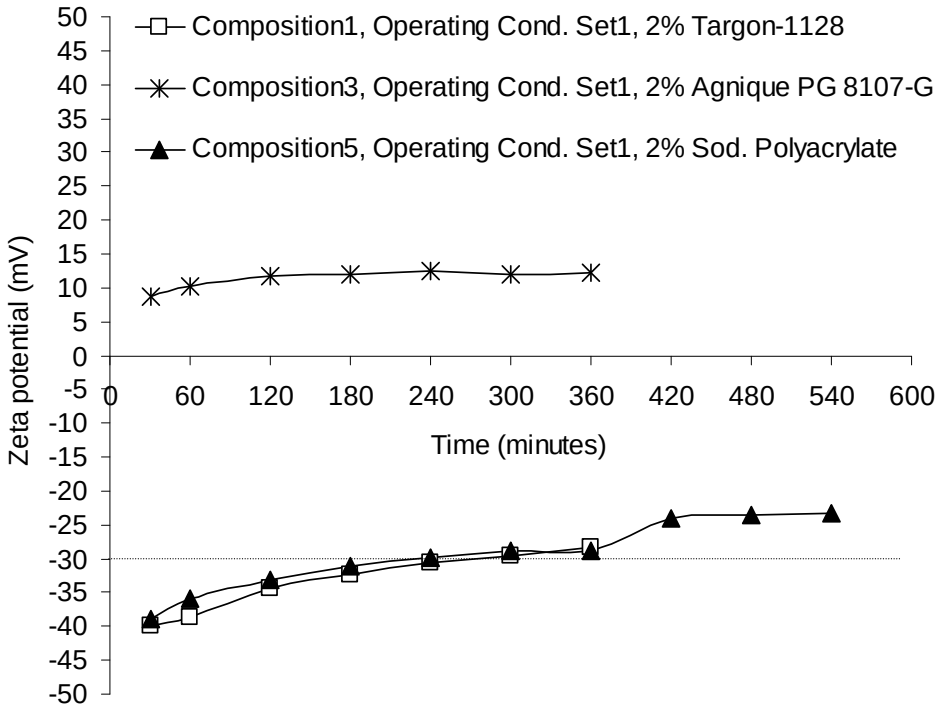

Fig. VI.4: Zeta potential versus time in the wet grinding of the compositions 1, 3 and 5 at set 1 of operating conditions.

For a reasonable stability in the particles, the zeta potential value of a particulate system, roughly, should be either below -30 mV or above +30 mV. The figure VI.4 explains that in case of composition 3, the value of zeta potential has been insufficient throughout the grinding process. This could be a strong reason that did not let the dispersion of this composition undergo an effective size reduction process. Foam that was observed in the dispersion of composition 3 may also be a likely reason that leads the dispersion of this composition to an inefficient size reduction process. The formation of foam is due to the composition of the dispersant (Agnique PG 8107-G) used in the composition 3.

The figure VI.4 explains that the dispersions of compositions 1 and 5 experience a gradual decrease in zeta potential with increasing grinding time. After six hours of the grinding, the minimum zeta potential in the dispersions of the composition 1 and 5 was noted -28.4. This explains that both dispersions have not been reasonably stable in six hours of the grinding.

The effect of materials (compositions of the dispersions) on product quality can be investigated by studying the characteristics of the final product prepared under similar grinding conditions. Dispersions of the compositions 1, 3 and 5 were ground under the same grinding conditions (set 1 mentioned in table VI.2). After six hours of the grinding process under the same operating conditions, the various characteristics of the products (final ground dispersions) of the mill were measured. The results are summarized in table VI.3.

Table VI.3: Effects of different compositions of materials on product characteristics (Case A)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 1	396	$122 < x < 1484$	-28.4	4.89	0.63	4.21	7833	No color change.
Composition 3	1731	$255 < x < 6439$	12.3	6.43	0.59	5.47	6157	No color change but foam formation.
Composition 5	339	$58.77 < x < 1718$	-28.9	8.59	0.77	7.59	5571	No color change.

The reported results of average particle size, range of particle size distribution, and stability (zeta potential) are based on measurements carried out with Zetasizer nano ZS.

The grinding process may cause breakage in grinding media and wear and tear in the grinding mill. If broken particles of grinding media (Zr_2O_3/ Y_2O_3) and grinding mill (stainless steal) are less than 100 nm, they can pass through the separating cartridge (100nm) and thus may affect purity of the product. Their presence in the ground product may be analyzed by detecting the quantity of Zr, Y and Fe with the help of an appropriate technique. All the results of impurity reported in this study are based upon inductive coupled plasma mass spectroscopy (ICP-MS). The values of specific energy reported show the amount of energy input during six hours of grinding to one kg of each material composition (dispersion). The results of physical appearance of the ground product are based upon close physical observation.

From the above discussion and the results in table VI.3, the following conclusions may be drawn for case A:

- The characteristics of final products of a milling process are dependent on composition of the materials.
- The composition 5 leads to a product that is better than the products 1 and 3 in terms of average particle size of the final product, stability and input of specific energy.
- The negative aspect with composition 5 is that it causes more breakage in the grinding medium and wear and tear in the mill as reflected from values of Zr, Y and Fr. Thus, on one hand the composition 5 causes the losses and breakage in grinding medium and stirred media mill and on the other hand, affect the impurity of the product.
- The comparison of composition 1 and 5 reflect that the composition 5 leads to better average particle size of the product. However, it is interesting to note that the specific energy input in case of composition 1 was 1.4 times more than in case of composition 5. The comparison implies that by selecting appropriate composition of a dispersion, even with less consumption of energy a desirable ground product may be achieved.
- The composition 3, that is based upon the dispersant, Agnique PG 8107-G, is inefficient in size reduction process. Figure V1.2 explains that the dispersant is not capable of keeping the particles dispersed during the grinding process. First peak in the size reduction process of the composition 3 (figure V1.2) points out that aggregation process takes place at about 2 hours. However, due to impact of continuous grinding the aggregates are broken later on. At this stage, the energy is utilized rather in breaking the aggregates and not in size reduction process. However, with the further grinding, the size of the particles starts to reduce again. But after a certain time, the particles again starts to aggregate. The instability of the particles is equally evident from zeta potential values of the system measured along the grinding process as mentioned in figure VI.4. For a reasonable stability in the particles, the zeta potential value of a particulate system, in general, should be either below -30 mV or above +30 mV. The composition 3, throughout the grinding process show a zeta potential between 5 and 15 mV, which is not sufficient in creating adequate repulsive forces between the particles.

VI.7.1.2 Case B

In case B, the results of the effects of two different compositions (2 and 6) of the materials (dispersions) on characteristics of the product are discussed. The wet grinding of the dispersions was carried out under the same operating condition of the mill (set 1, table VI.2). The compositions of the dispersions differ in terms of type of added dispersants. The dispersants Targon-1128 and sodium polyacrylate were employed in the compositions 2 and 6 respectively. The concentrations of the

dispersions and the proportion of added dispersants in both dispersions were kept same (i.e. 8% of the weight of the $CaCO_3$).

The figures VI.5 and VI.6 present the results of size reduction process in above mentioned dispersions along time and specific energy. Till 4th hour of the grinding process, both dispersions show almost similar trend in size reduction. However, when the particles approach size about 200 nm, the dispersion of composition 2 (with Targon-1128) starts to aggregate. After 4th hour, an ascending trend in the particle size of the dispersion of composition 2 may be observed clearly in the figures VI.5 and VI.6.

It may also be concluded from figures VI.5 and VI.6 that Targon-1128 does not remain efficient in stabilizing the particles after 4th hour of the grinding process when the average particle size of the product is about 200nm. This may be due to colloidal forces that start to influence the dispersions stability.

Figure VI.6 explains that in composition 2, the specific energy from approximately 3500 to 7000 KJ/Kg is used inefficiently after 4th hour of grinding. No size reduction process takes place in this interval. This highlights the loss of almost 50% of specific energy in the dispersion of composition 2.

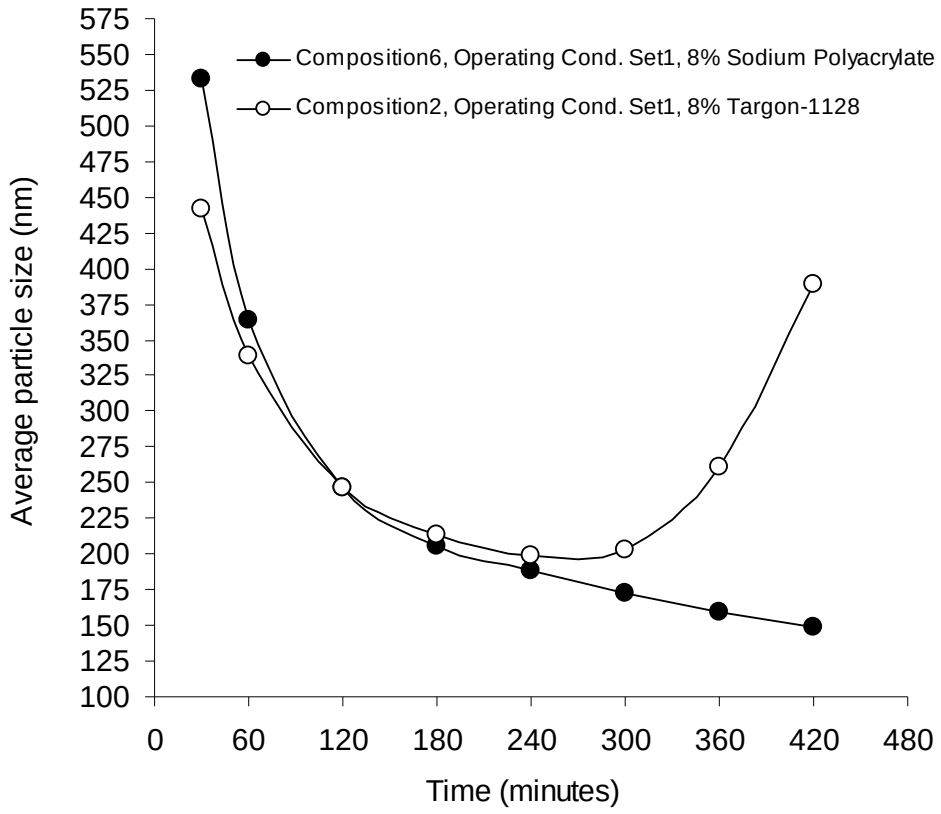

Fig. VI.5: Progression of size reduction process against time in the compositions 6 and 2 at set 1 of operating conditions.

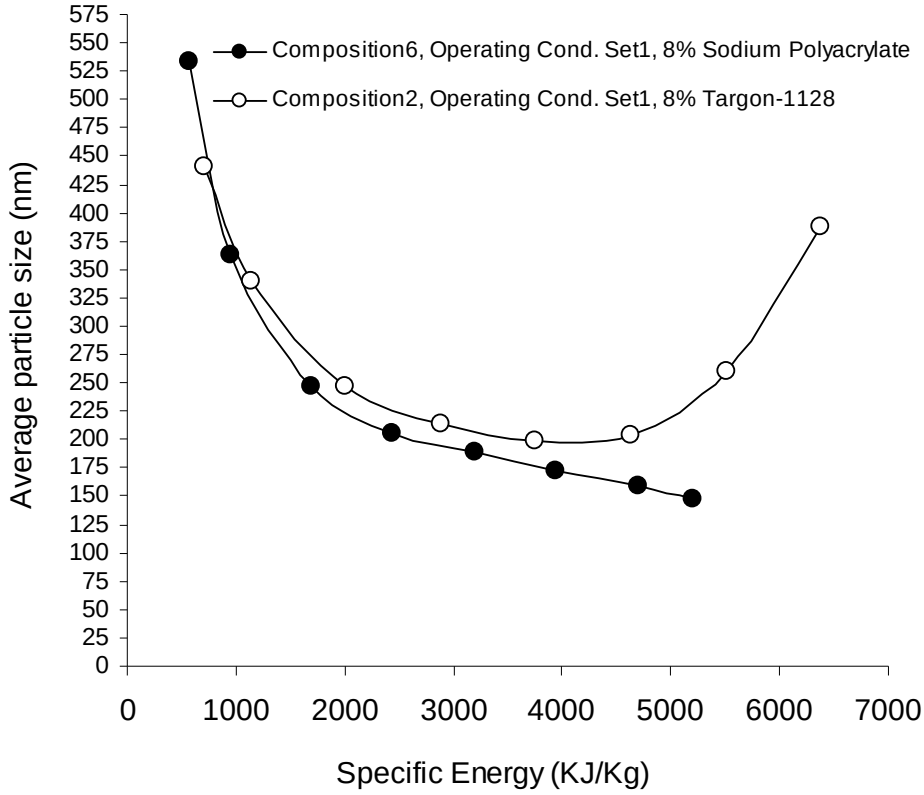

Fig. VI.6: Progression of size reduction process against specific energy in the compositions 6 and 2 at set 1 of operating conditions.

In order to understand the different behavior of the dispersions of composition 2 and 6 under the same operating conditions of the grinding, the zeta potential studies were carried out at different intervals of time during grinding processes. The results are presented in figure VI.7.

The figure VI.7 explains that the dispersions of compositions 2 and 6 experience a gradual decreasing trend in the zeta potential with grinding time. The zeta potential in case of the dispersion of composition 6 remains below -30 mV throughout the grinding process. Whereas in case of dispersion of composition 2, the zeta potential remains below -30 mV in first four hours of grinding where no aggregation is observed.

However, after 4^{th} hour of grinding the value of zeta potential gets slightly above -30 mV. It is the stage where aggregation in the dispersion of composition 2 is observed. This highlights that even small increase in the zeta potential from -30 mV may seriously affect the size reduction process.

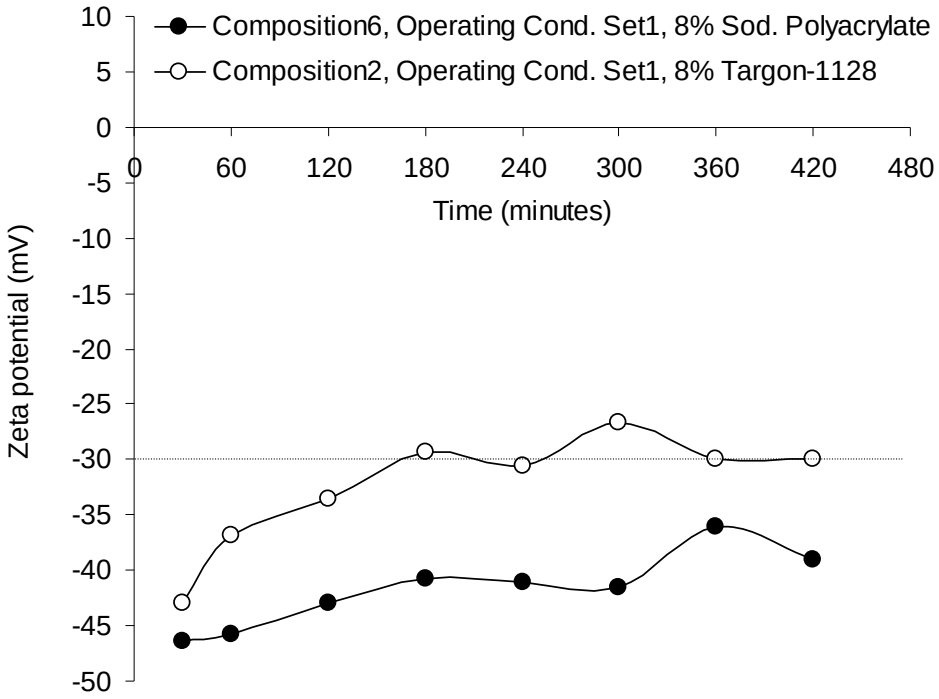

Fig. VI.7: Zeta potential versus time in the wet grinding of the compositions 2 and 6 at set 1 of operating conditions.

As already discussed, the effect of materials (compositions of the dispersions) on product quality can be investigated by studying the characteristics of the final product prepared under similar grinding conditions. Dispersions of the compositions 2 and 6 were ground under the same grinding conditions (set 1, table VI.2). After six hours of the grinding process under the same operating conditions, the various characteristics of the products (final ground dispersions) of the mill were measured. The results are summarized in table VI.4.

Table VI.4: Effects of different compositions of materials on product characteristics (Case B)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 2	261	28.21 < x < 1718	-29.9	19.08	1.59	4.10	5509	No color change.
Composition 6	160	28.21 < x < 531	-36	10.36	0.97	4.77	4695	No color change.

It is observed that the grinding of the dispersion based on composition 6 produces the product that is distinctively better in terms of particle size, particle size range, stability, breakage of grinding media, and input of specific energy. However, it seems that the composition 6 causes a little more wear and tear in the mill as clear from the degree of impurity because of Fe.

VI.7.1.3 Case C

In case C, the results of the effects of two different compositions (2 and 6) of the materials (dispersions) on characteristics of the product are discussed like in case B. The difference in case B and C is that the grinding process was carried out at set 2 of operating conditions instead of set 1. As already discussed, the dispersants Targon-1128 and sodium polyacrylate were employed in the compositions 2 and 6 respectively. The concentrations of the dispersions and the proportion of added dispersants in both dispersions were kept same (i.e. 8 % of the weight of the $CaCO_3$).

The figure VI.8 and VI.9 show the progression of grinding processes in above mentioned dispersions along time and specific energy respectively. A smooth size reduction process is observed in case of the dispersion of composition 2. The particle size gradually decreases with increasing grinding time in the dispersion of composition 2. In the dispersion of composition 6, it was observed that:

- The particle size decreases in 1^{st} hour of grinding.
- From 1^{st} to 4^{th} hours of grinding an aggregation is observed.
- From 4^{th} to 7^{th} hours of grinding the particle size again starts to decrease, perhaps, due to breakage of agglomerates.
- Till average particle size of 250 nm approximately, the grinding process takes place smoothly. The grinding time and specific energy input corresponding to this stage are 1 hour and 4000 KJ/Kg approximately.
- Specific energy input from 2^{nd} to 7^{th} hour of grinding process is about 22000 KJ/Kg.
- This specific energy input that is used effectively in size reduction process is 4000 KJ/Kg whereas the specific energy that is inefficiently provided to system is 22000KJ/Kg. It means 5.5 times energy is utilized inefficiently.

The comparison of the grinding process of composition 2 and 6 carried under the same operating conditions highlights the importance of the composition of the materials in the wet grinding process. It is evident that using the composition 2, the effective grinding process can be achieved only in first grinding hour. Later on, the energy is utilized, likely, against the aggregation process and not in breaking of particles. Whereas, in case of composition 6, the smooth grinding process is observed. All the specific energy is utilized effectively in size reduction process.

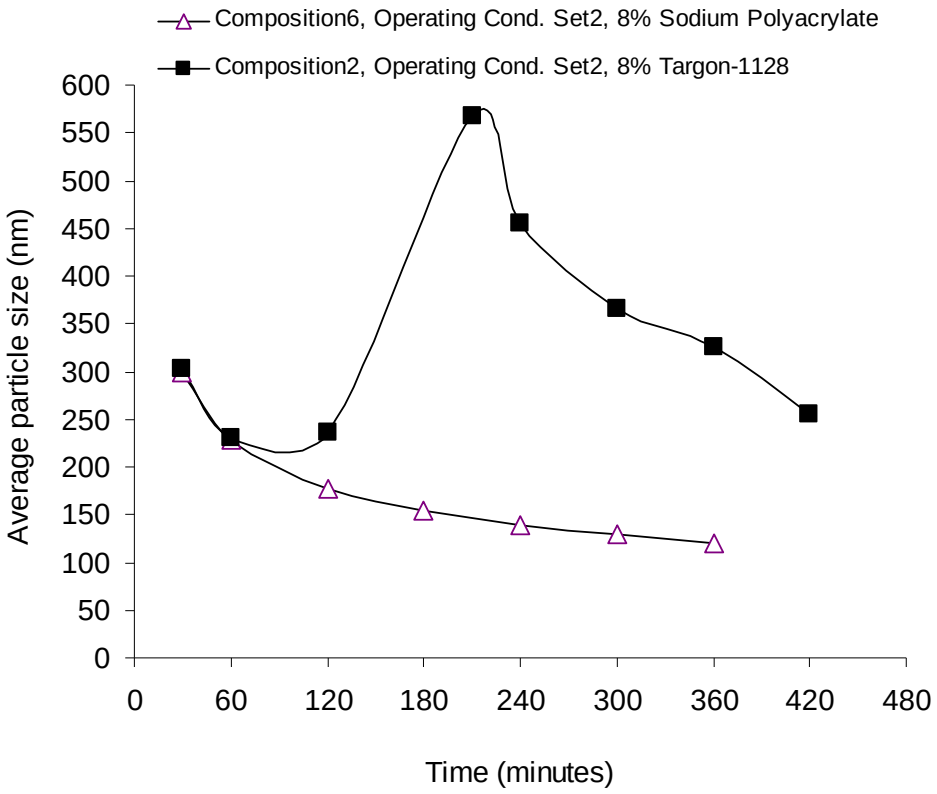

Fig. VI.8: Progression of size reduction process against time in the compositions 2 and 6 at set 2 of operating conditions.

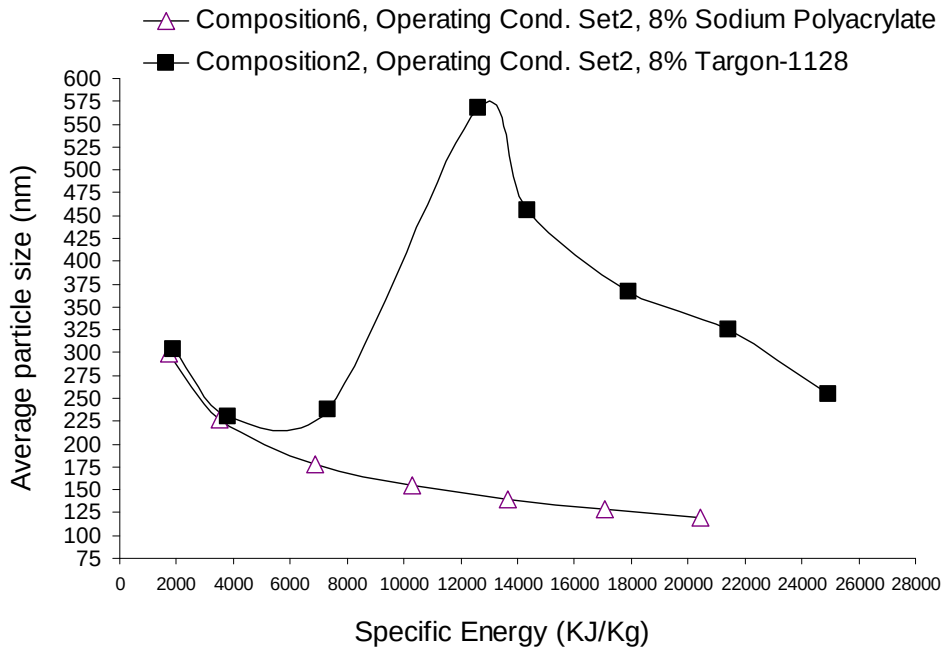

Fig. VI.9: Progression of size reduction process against specific energy in the compositions 2 and 6 at set 2 of operating conditions.

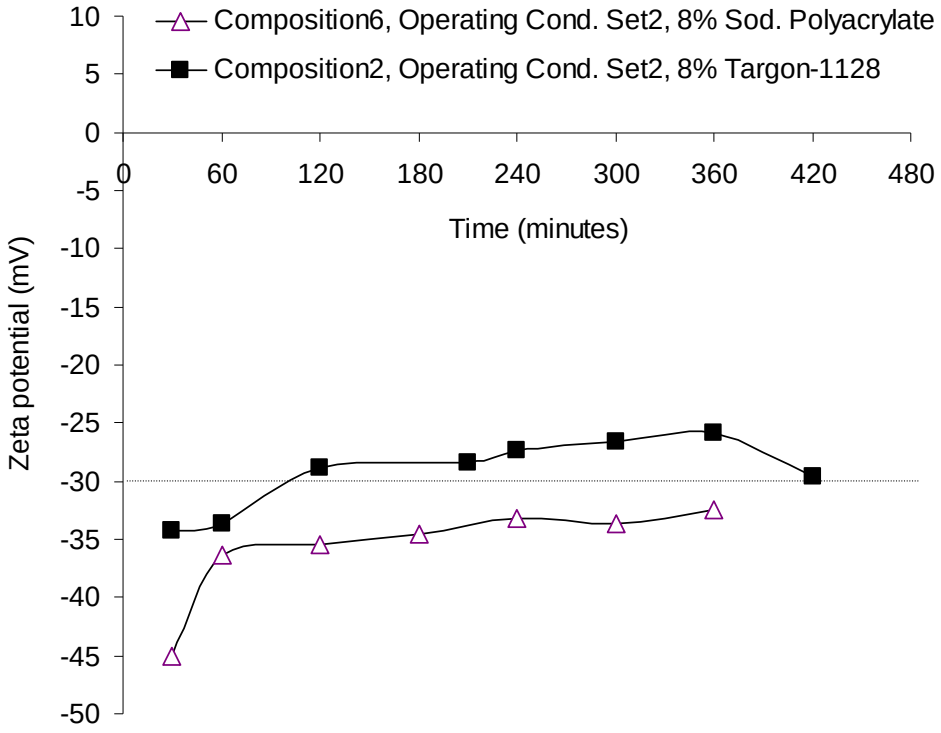

Fig. VI.10: Zeta potential versus time in the wet grinding of the compositions 2 and 6 at set 2 of operating conditions.

The efficient grinding process in the dispersion of composition 6 and inefficient grinding process in the dispersion of composition 2 carried out under the same operating conditions can be understand by zeta potential study as mentioned in the figure VI.10.

The zeta potential study explains that in the dispersion of composition 6, the zeta potential remains less than -30 mV throughout the grinding process whereas in the dispersion of composition 2, the zeta potential after 2nd grinding hours become higher than -30 mV. This explains how the grinding process and the characteristics of resulting products are dependent on the material compositions used in the grinding process. After six hours of the grinding process under the same operating conditions (set 2 of the operating conditions of the mill), the various characteristics of the products (final ground dispersions) formed with dispersions of compositions 2 and 6 were measured. The results have been summarized in table VI.5.

Table VI.5: Effects of different compositions of materials on product characteristics (Case C)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 2	326	28.21< x <6439	-25.8	114.01	8.43	17.78	21408	Silver gray color is observed.
Composition 6	120	37.84< x <531.2	-32.4	91.57	7.00	17.14	20431	Silver gray color is observed.

The comparison explains that the grinding process carried out with the dispersion of composition 6 leads to a product that is comparatively good in terms of average particle size, particle size range, and zeta potential. The dispersions of both compositions cause breakages in grinding media however the loss of grinding media in case of composition 6 is less than in case of 2 as mentioned by the values of Zr and Y. Similarly, both compositions cause wear and tear in the grinding mill. This is evident from values of Fe and change in color of the dispersions at the end of the process. However, the wear and tear in the mill due to composition 6 is less than due to composition 2. The composition 2 in terms of specific energy input is equally better than the composition 6.

VI.7.1.4 Case D

In case D, the results of the effects of two compositions (5 and 6) on product characteristics are discussed. Both dispersions were ground at operating conditions set 1. They have the same concentrations. They differed in added proportions of sodium polyacrylate that were 2 and 8 % respectively.

Figures VI.11 and VI.12 show that the dispersion of composition 5 (with 2% sodium polyacrylate) starts experiencing aggregation after 2 hours of grinding when average size of the particles is about 230 nm corresponding about 2100KJ/Kg specific energy input.

Figure VI.13 explains that in the dispersion of composition 5, the zeta potential remains considerable lower than -30 mV till second hour of grinding, whereas in the third hour of grinding, it approaches -30 mV likely to cause aggregation.

The dispersion with composition 6 undergoes a smooth size reduction process throughout. Its zeta potential remains though out the grinding process reasonable below -30 mV.

Table VI.6 compares the product characteristics of composition 5 and 6 after 6 hours of grinding under set 1.

Table VI.6: Effects of different compositions of materials on product characteristics (Case D)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 5	339	58.77 < x < 1718	-28.9	8.59	0.77	7.59	5571	No color change.
Composition 6	160	28.21 < x < 531	-36	10.36	0.97	4.77	4695	No color change.

It is observed that the dispersion of composition 6 distinctively produces a better product in terms of average particle size, particle size range, stability (zeta potential), impurities due to iron loss, and specific energy input.

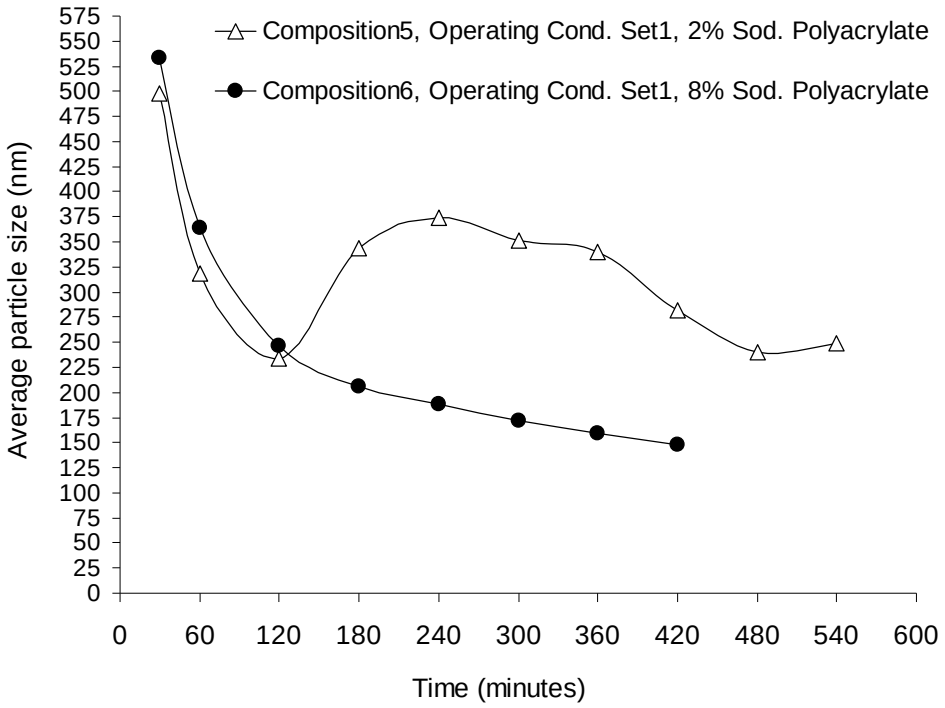

Fig. VI.11: Progression of size reduction process against time in the compositions 5 and 6 at set 1 of operating conditions.

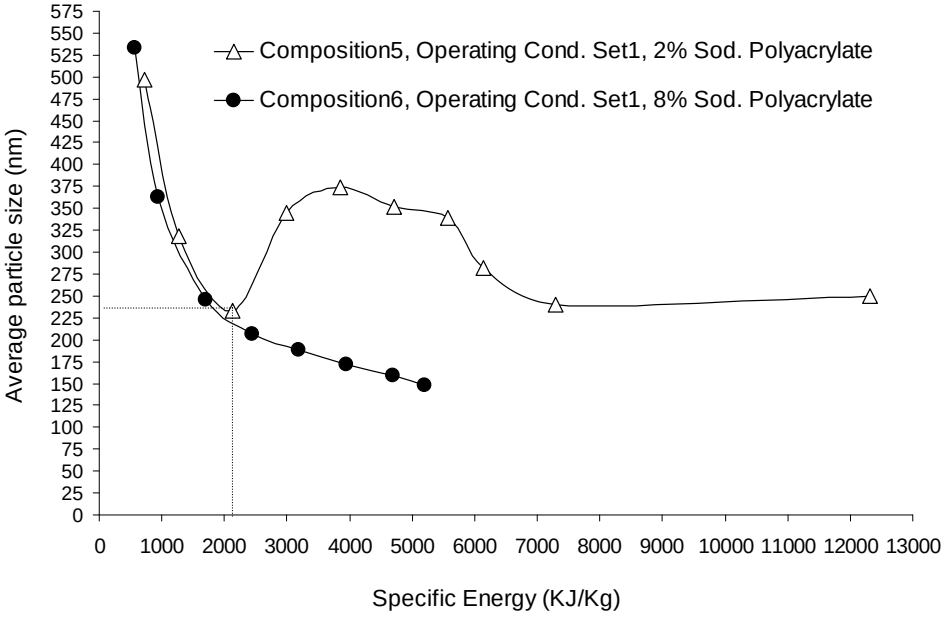

Fig. VI.12: Progression of size reduction process against specific energy in the compositions 5 and 6 at set 1of operating conditions.

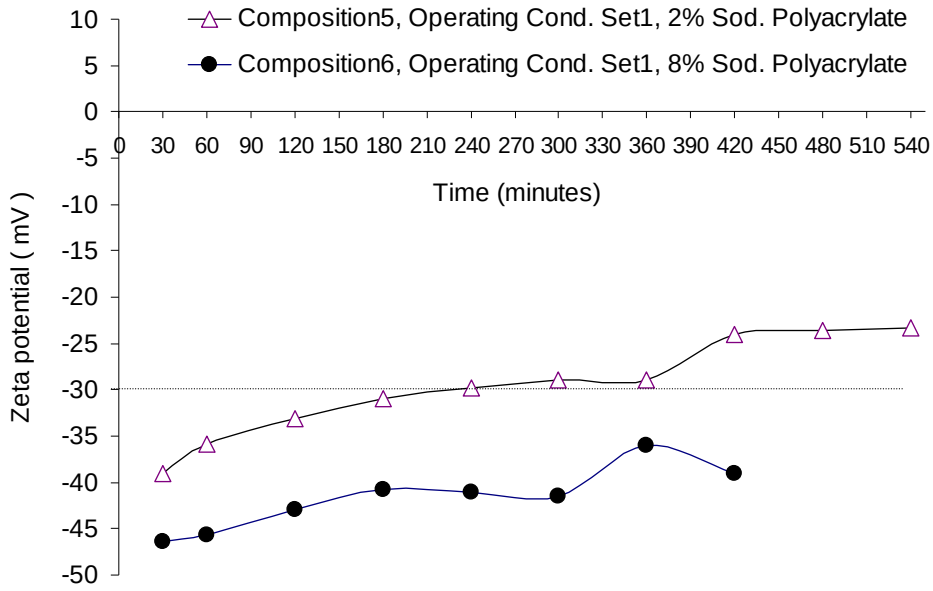

Fig. VI.13: Zeta potential versus time in the wet grinding of the compositions 2 and 6 at set 2 of operating conditions.

VI.7.1.5 Case E

In case E, the results of the effects of two compositions (1 and 2) on product characteristics are discussed. Both dispersions were ground at operating conditions set 1. They had the same concentrations. They differed in added proportions of Targon-1128 that were 2 and 8 % respectively.

Figure VI.14 and VI.15 show that the dispersion of composition 1 (with 2% Targon-1128) starts experiencing aggregation after 1 hours of grinding when average size of the particles is about 350 nm corresponding about 1500 KJ/Kg specific energy input. The zeta potential studies of the dispersions of compositions 1 and 2, as in figure VI.16, explain that till second hour of grinding, both the dispersions shows almost similar values of zeta potentials, reasonably below -30 mV. However, from 3rd hour of grinding, the dispersion of composition 2 shows comparatively higher values of zeta potential. Table VI.7 compares the product characteristics of composition 1 and 2 after 6 hours of grinding under set 1 of operating conditions.

Table VI.7: Effects of different compositions of materials on product characteristics (Case E)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 1	396	122 < x < 1484	-28.4	4.89	0.63	4.21	7873	No color change.
Composition 2	261	28.21 < x < 1718	-29.9	19.08	1.59	4.10	5509	No color change.

The table VI.7 shows that in the dispersion of composition 2 using less specific energy out put better average particles size of the product may be achieved. However, using the dispersion based on composition 1, narrow particle size distribution and low values of impurities may be achieved in the

products. Moreover, it is clear that the stability of dispersion of composition 2 is better than of composition 1.

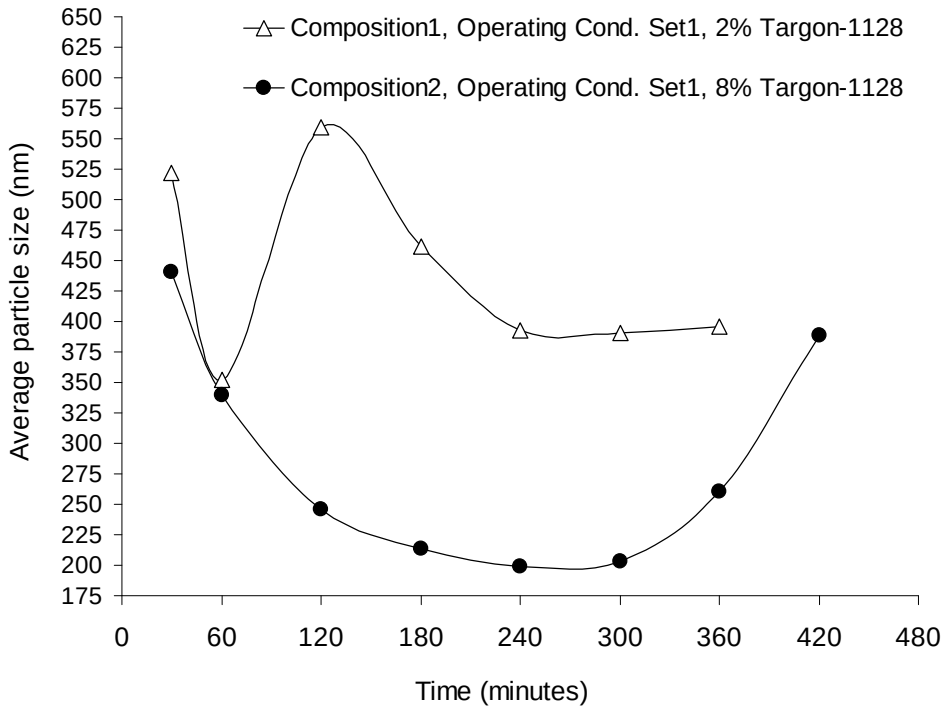

Fig. VI.14: Progression of size reduction process against time in the compositions 1 and 2 at set 1 of operating conditions.

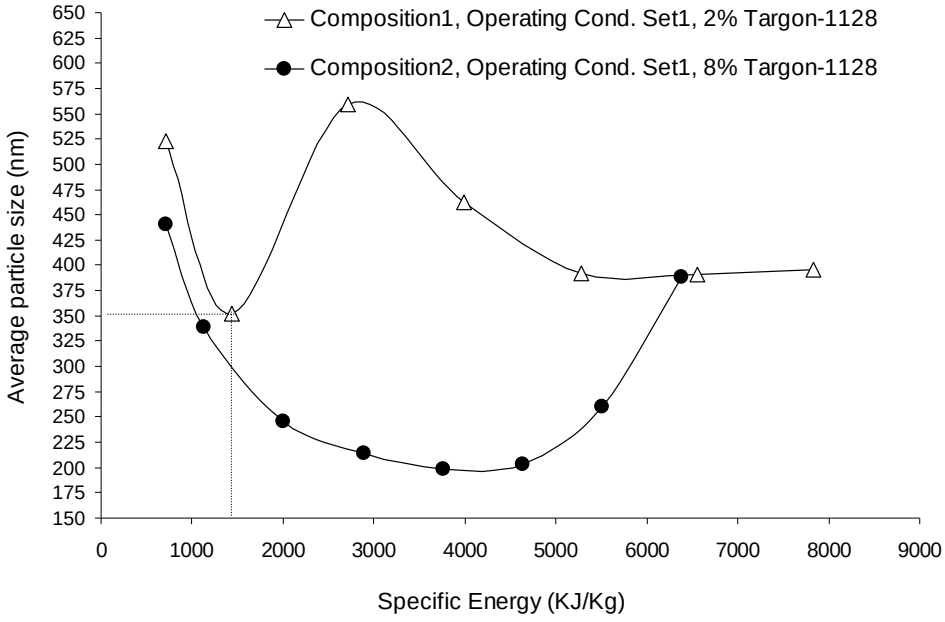

Fig. VI.15: Progression of size reduction process against specific energy in the compositions 1 and 2 at set 1of operating conditions.

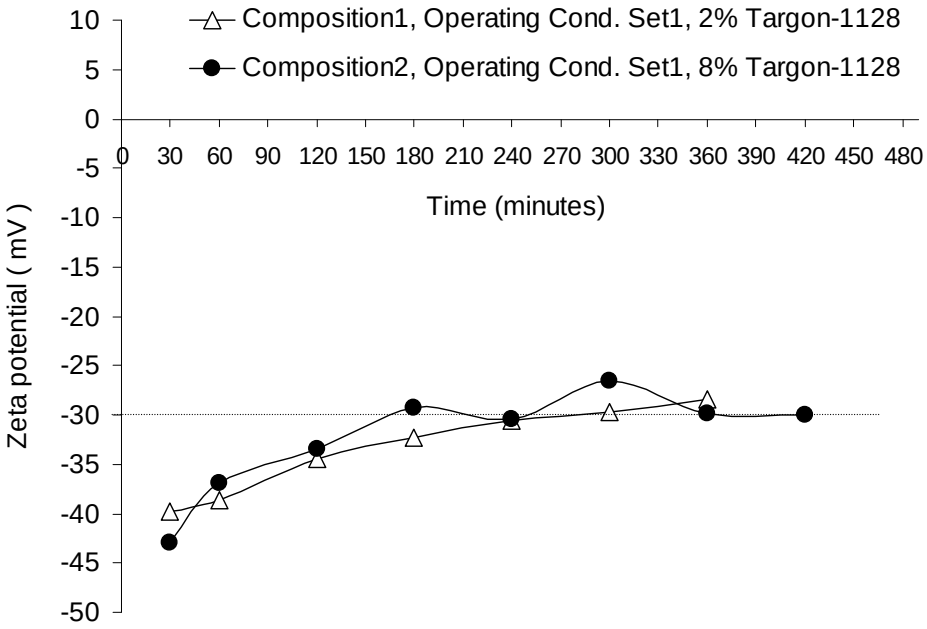

Fig. VI.16: Zeta potential versus time in the wet grinding of the compositions 1 and 2 at set 1 of operating conditions.

VI.7.1.6 Case F

In case F, the results of the effects of four compositions (7, 8, 6, 9) of the dispersions that vary in terms of concentrations have been discussed on characteristics of the final ground product. Table VI.1 provides the details of the compositions. All the four dispersions of compositions 7, 8, 6, 9 were ground under the set 1 of operating conditions of the mill (table VI.2). The grinding results of the above mentioned dispersions have been presented in the figure VI.17 and VI.18.

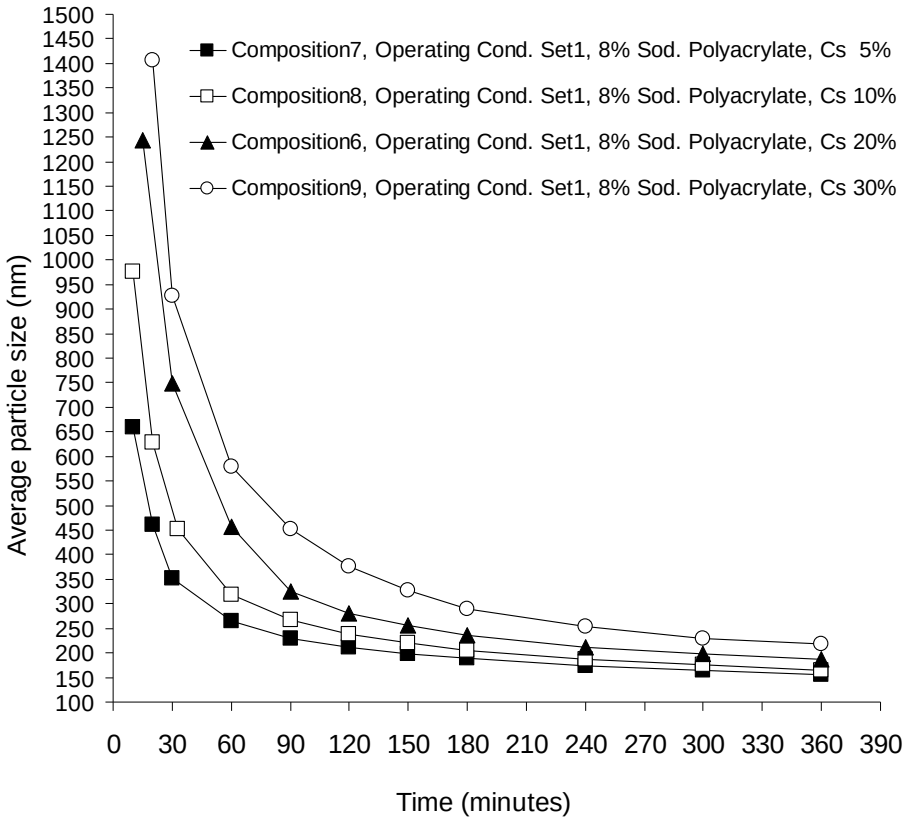

Fig. VI.17: Progression of size reduction process against time in the compositions 7, 8, 6, 9 at set 1 of operating conditions.

All the four compositions that are based upon sodium polyacrylate show a smooth size reduction process. No aggregation is observed in the grinding processes of above mentioned dispersions. It is further observed that the use of dilute dispersions may lead to better particle sizes of the final product.

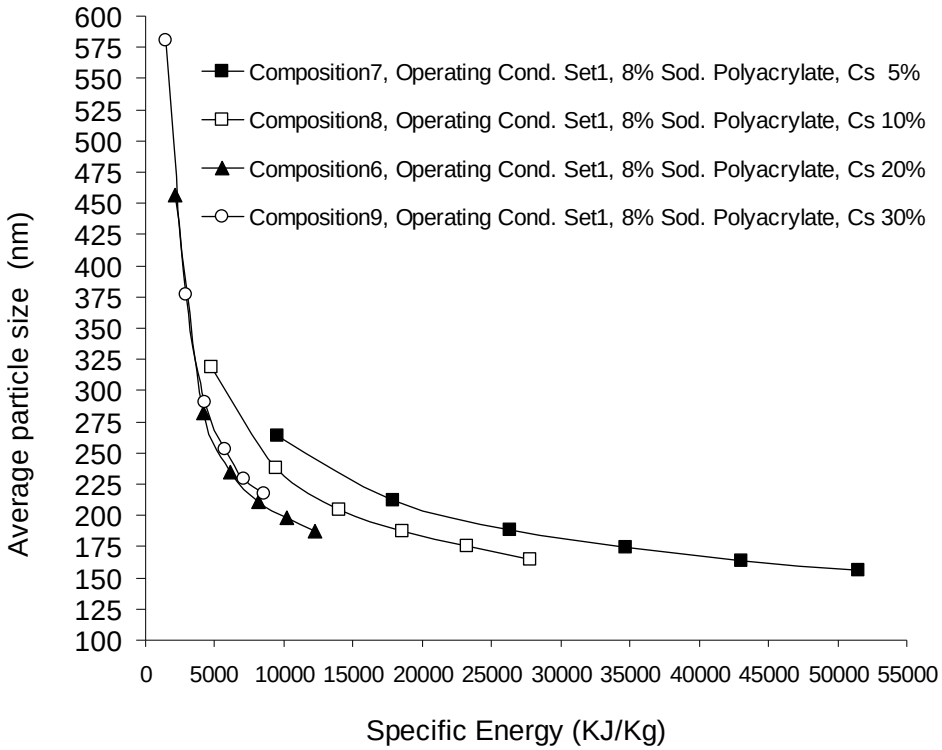

Fig. VI.18: Progression of size reduction process against specific energy in the compositions 7, 8, 6 and 9 at set 1 of operating conditions.

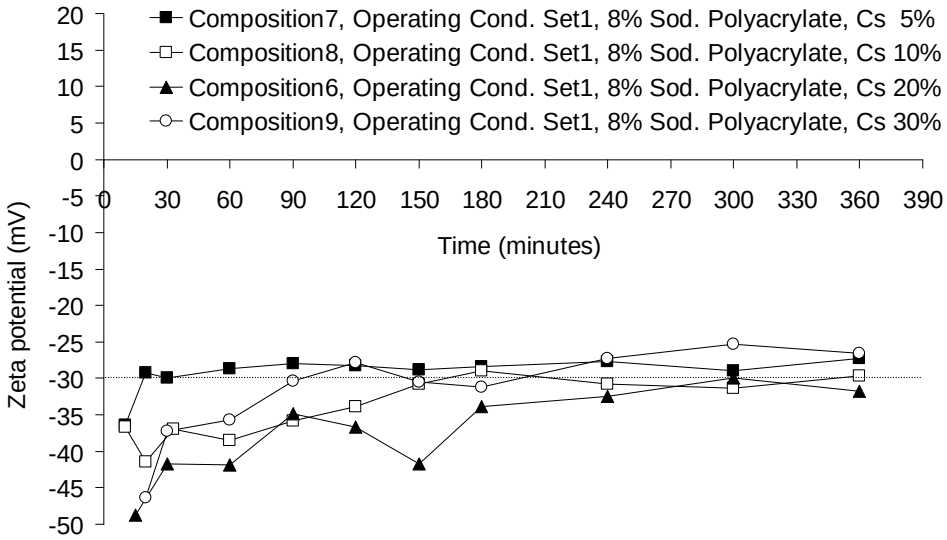

Fig. VI.19: Zeta potential versus time in the wet grinding of the compositions 7, 8, 6, 9 at set 1 of operating conditions.

The results of the zeta potentials in case F have been reported in the figure VI.19. A fluctuation is observed in the zeta potential potentials of these compositions. However, no aggregation is observed at throughout the grinding process. The product characteristics of the grinding products prepared from the compositions 7, 8, 6, 9 were measured. The results are given in table VI.8.

Table VI.8: Effects of different compositions of materials on product characteristics (Case F)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Composition 7	156	28.21 < x < 825	-27.3	12.26	1.11	3.85	51462	No color change
Composition 8	165	28.21 < x < 721.4	-29.6	11.27	1.10	3.28	27776	No color change
Composition 6	187	5.75 < x < 712.4	-31.7	13.33	1.15	7.44	12228	No color change
Composition 9	218	37.84 < x < 825	-26.6	16.12	1.14	8.24	8544	No color change

It is observed that the dispersion based upon composition 7 produces finer particles comparative to other compositions. It may be realized that average particle size from the composition 7 to 9 increases. In other words, the increase in dilution in dispersions favor in achievement of finer particles.

Kwade (2002) explained that product of the stress number (*SN*) and the stress intensity (*SI*) is proportional to the specific energy (E_m) of the mill. i.e.

$$E_m \alpha \ SN.SI \qquad \text{…….. (6.2)}$$

Under similar operating conditions of the mill, the stress intensity is constant and, therefore, the specific energy is determined by stress number which depends upon number of media contacts (N_c), by the probability that a particle is caught and sufficiently stressed at a media contact (P_s) and by the number of feed particles inside the mill (N_p).

$$SN = \frac{N_c P_s}{N_p} \qquad \text{…….. (6.3)}$$

At same values of N_c and P_s as in case of the dispersions of compositions 7,8,6 and 9, the stress number and ultimately stress energy is inversely proportional to the number of feed particles inside the mill. In other words, the stress energy is inversely proportional to the concentration of the dispersion. Thus, it may be explained why the specific energy input from composition 7 to 9 (i.e. from C_s 5% to 30%) decreases gradually.

VI.7.2 Effects of operating conditions of the mill on product characteristics

This section analyzes how product characteristics are affected if a material is ground at different operating conditions of the grinding mill. Two sets of operating conditions, as mentioned in table VI.2 have been considered in this study. The experimental results have been discussed in two cases.

VI.7.2.1 Case G

This case discusses the grinding of composition 6 (20% m/m aqueous dispersion of $CaCO_3$ added with 8% of sodium polyacrylate by the weight of $CaCO_3$) carried out under two different sets of operating conditions (table VI.2). The grinding results of the dispersion of composition 6 carried under operating set 1 and set 2 have been shown in figures VI.20 and VI.21 against time and specific energy.

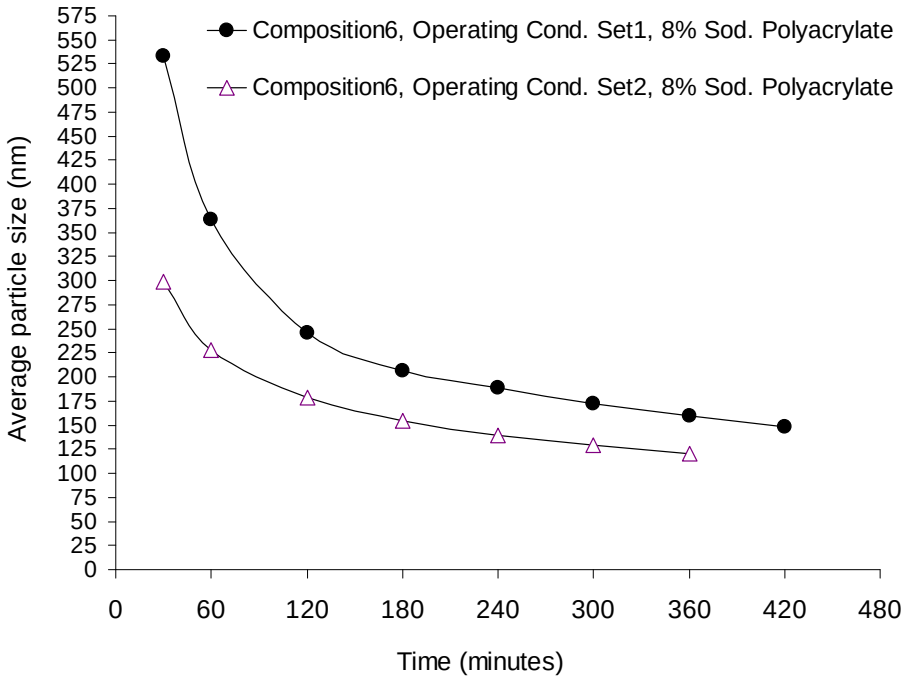

Fig. VI.20: Progression of size reduction process against time in the compositions 6 at set 1 and 2 of operating conditions.

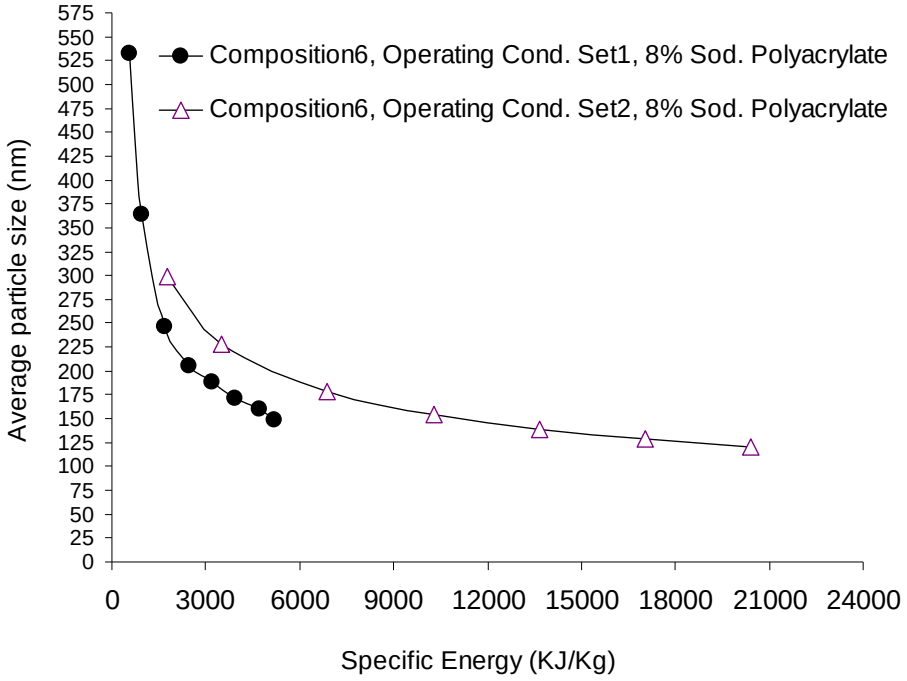

Fig. VI.21: Progression of size reduction process against specific energy in the compositions 6 at set 1 and 2 of operating conditions.

Figure VI.20 and VI.21 explain that the dispersions of composition 6 undergoes a smooth size reduction process both in set 1 and set 2 of operating conditions. No aggregation is observed under both sets of operating conditions.

Figure VI.20 demonstrates that the set 2 as compared to set 1of operating conditions, yield smaller particles under the same interval of time. However, figure VI.21 explains that specific energy input in case of set 2 is quite higher than in case of set 1. For example, in order to produce the product of an average particle size of about 145 nm, the set 2 requires specific energy more than 2 times than in case of set 1. It means in set 2, the half of the energy is utilized inefficiently. A part of this surplus energy is utilized in rising the temperature of the product whereas some part is likely used in causing breakage in grinding media and wear and tear in the grinding mill.

The change in color of the dispersion from white to white with grey tone support that the surplus energy leads to wear in tear in the mill generating fine iron particles of grey color that finely mix up with the product giving it a grey tone.

The figure VI.22 show the zeta potentials of the dispersions in the grinding process carried at set 1 and set 2 of operating conditions.

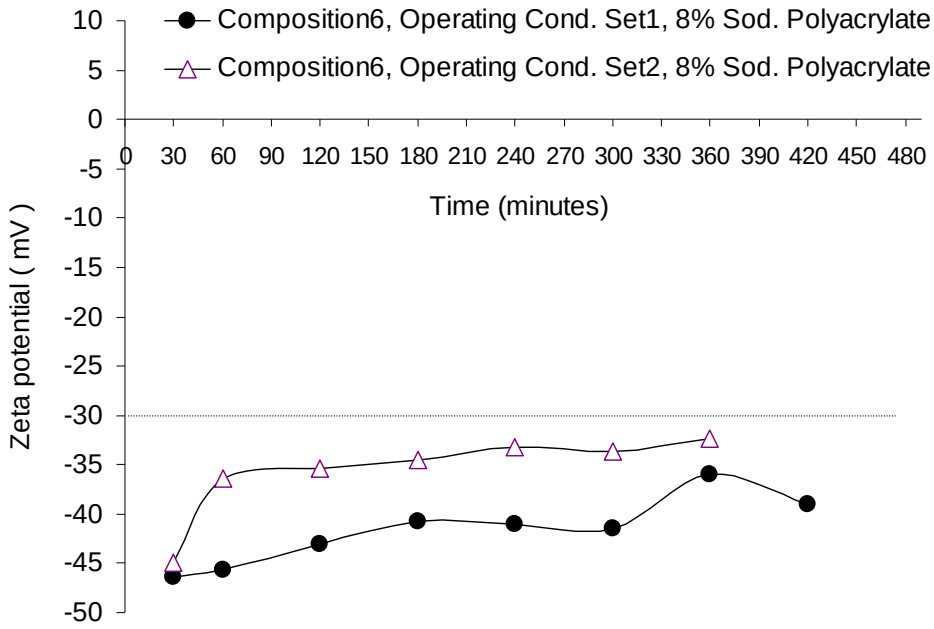

Fig. VI.22: Zeta potential versus time in the wet grinding of the compositions 6 at set 1 and 2 of operating conditions.

Figure VI.22 explains that the stability of the dispersion of composition 6 when it was ground under operating set 1 is better than in set 2. The change in values of zeta potential under set 2 may be due to addition of Fe particles generated because of wear and tear in the mill.

After about six hours of the grinding process under set 1 and set 2 of operating conditions of the mill, the various characteristics of the products were measured. The results are summarized in table VI.9.

Table VI.9: Effects of different compositions of materials on product characteristics (Case G)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Set 1	160	28.21 < x < 531	-36	10.36	0.97	4.77	4695	No color change.
Set 2	120	37.84< x <531.2	-32.4	91.57	7.0	17.14	20431	Silver gray color is observed

Table VI.9 explains that using set 2 better average particle size can be achieved in the dispersion of composition 6. The distribution of produced particles is also slightly better (narrow) in case of set 2. However, the set 2 requires considerably high specific energy input during six hours of grinding. About 4.3 times more specific energy input is required in grinding under set 2 than in set 1. Another disadvantage of the operating set 2 is that it causes 3.6 times more wear and tear in the mill and about 7.2-8.8 times more loss in grinding media.

VI.7.2.2 CASE H

This case discusses the grinding of composition 2 (20% m/m aqueous dispersion of $CaCO_3$ added with 8% of Targon-1128 by the weight of $CaCO_3$) carried out under two different sets of operating conditions (table VI.2). The grinding results of the dispersion of composition 6 carried under operating set 1 and set 2 have been shown in figures VI.23 and VI.24 against time and specific energy. Figure VI.23 explains that the dispersion of composition 2 when ground under set 1 of operating conditions, follows a smooth size reduction process till 4^{th} hour of grinding that corresponds to an average particle size of about 200 nm. Thereafter, the particles in the dispersion start to aggregate as indicated by the rise in the curve of average particle size. The process of aggregation, under set 2 is observed after 2 hours of grinding that corresponds to an average particle size of about 231 nm. From 2nd to 7th hours of grinding, it seems that the agglomerate starts to break with increasing grinding time. Figure VI.24 explains that about 4000 KJ/kg of specific energy input, the size reduction process both under set 1 and set 2 takes place efficiently. Thereafter, the specific energy is not utilized efficiently in reducing the size of the particles. In set 2, the speed of rotation of stirrer in grinding chamber is comparatively high. This results in high specific energy input during grinding process. A part of this energy is utilized in breaking the agglomerates of the dispersion as indicated by a gradual decrease in curve from 4^{th} to 7^{th} grinding hour in set 2, figure VI.23. Some part of the energy is utilized equally in rising the temperature of the product and the mill. Moreover, some energy is utilized causing the wear and tear in the grinding media and the mill. The change in color of the dispersion, from white to white with grey tone, supports that a part of the energy leads to wear and tear in the mill generating fine iron particles of grey color that finely mix up with the product giving it a grey tone.

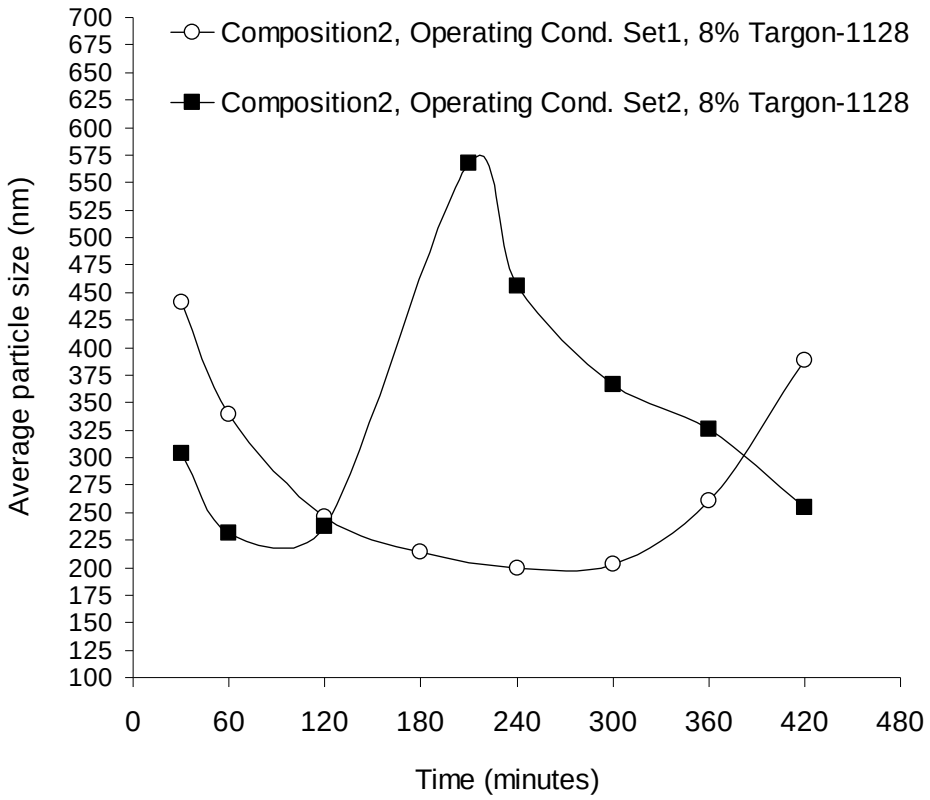

Fig. VI.23: Progression of size reduction process against time in the compositions 2 at set 1 and 2 of operating conditions.

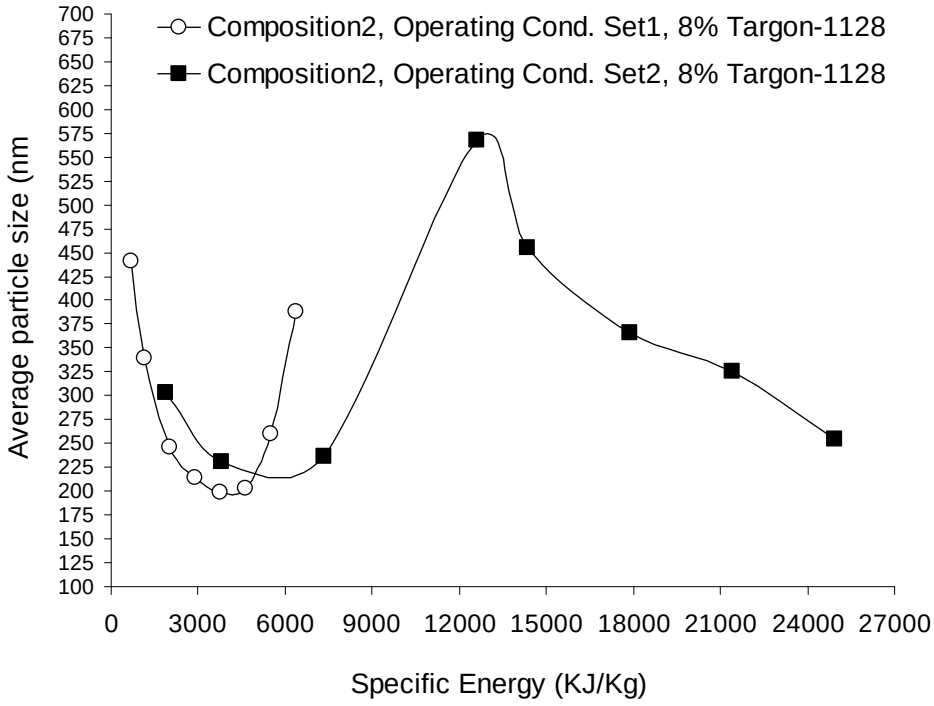

Fig. VI.24: Progression of size reduction process against specific energy in the compositions 6 at set 1 and 2 of operating conditions.

The study of zeta potential of the dispersion of composition 2 under the set 1 and set 2 of the operating conditions have been shown in the figures VI.25.

The reason of aggregation of in the dispersion ground under set 2 of operating conditions can be explained on the basis of figure VI.25 that explains that the zeta potential of the dispersion become higher than -30 mV from 2nd hour of grinding till end of the process.

In the dispersion treated under set 1, the aggregation seems to start after 4th hour of grinding (figure VI.23). However, the zeta potential study for this dispersion shows that the zeta potential of the dispersion gets into unstable zone (i.e. higher than -30 mV) from 3rd hour of grinding. The reason of this discrepancy cannot be explained with certainty. A possible reason may be that the sample considered for zeta potential measurement was having relatively higher proportion of finer particles due to homogenization problem.

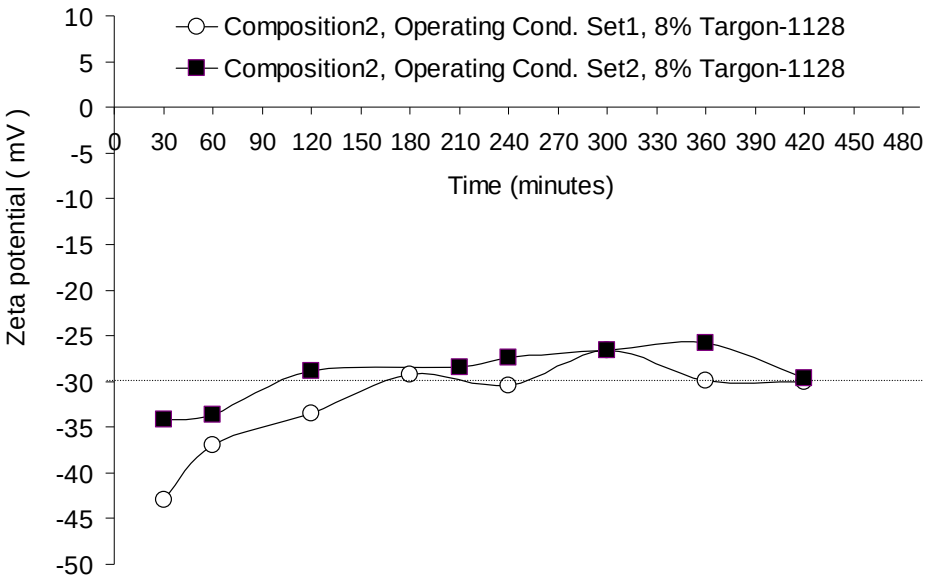

Fig. VI.25: Zeta potential versus time in the wet grinding of the compositions 2 at set 1 and 2 of operating conditions.

After about six hours of the grinding process under set 1 and set 2 of operating conditions of the mill, the various characteristics of the products produced from dispersion of composition 2 were measured. The results are summarized in table VI.10.

Table VI.10: Effects of different compositions of materials on product characteristics (Case H)

Material	Average particle size (nm)	Range in nm of particle sizes distribution, (x)	Stability (zeta potential) mV	Impurity (mg/kg) Zr	Y	Fe	Specific energy KJ/Kg	Physical appearance
Set 1	261	28.21 < x < 1718	-29.9	19.08	1.59	4.10	5509	No color change.
Set 2	326	28.21< x <6439	-25.8	114.01	8.43	17.78	21408	Silver gray color is observed

Table VI.10 explains that the dispersion of composition 2 ground under set 1 results in the product that is better in particle size, particle size range, stability, and wear and tear in grinding media and mill and specific energy input.

VI.7.3 Effects of measurement techniques on product characteristics

As discussed by Ishikawa (1990), a measurement technique plays an important role in measurement of product characteristics. The matter is rather important in case of particle sizing during wet grinding processes. The particle sizing techniques such as acoustic attenuation spectroscopy, dynamic light scattering and laser diffraction are based upon some approximations and assumptions. During a wet grinding process, when particles enter from micron to colloidal size range, some assumptions and approximations might not remain valid resulting in poor or wrong measurement of characteristics of the product.

The particle sizing of the dispersions of compositions no. 7, 8, 6 and 9 during wet grinding process was carried out with technique of dynamic light scattering and acoustic attenuation spectroscopy. Four dispersions were treated under set 1 of the operating conditions. The compositions of the dispersions have been given in table VI.1. The particle sizing by means of dynamic light scattering of above dispersions revealed that by using dilute dispersions the product with fine particle may be produced more easily by means of wet grinding. Figure VI.26 explains this.

The particle sizing by means of acoustic attenuation spectroscopy of above dispersion brings information entirely opposite. Acoustic attenuation spectroscopy explains that by using concentrated dispersions the product with fine particle may be produced more easily. Figure VI.27 explains it.

In figure VI.28, the trends generated by both the techniques have been compared. Both techniques reports entirely different characteristics of the ground product.

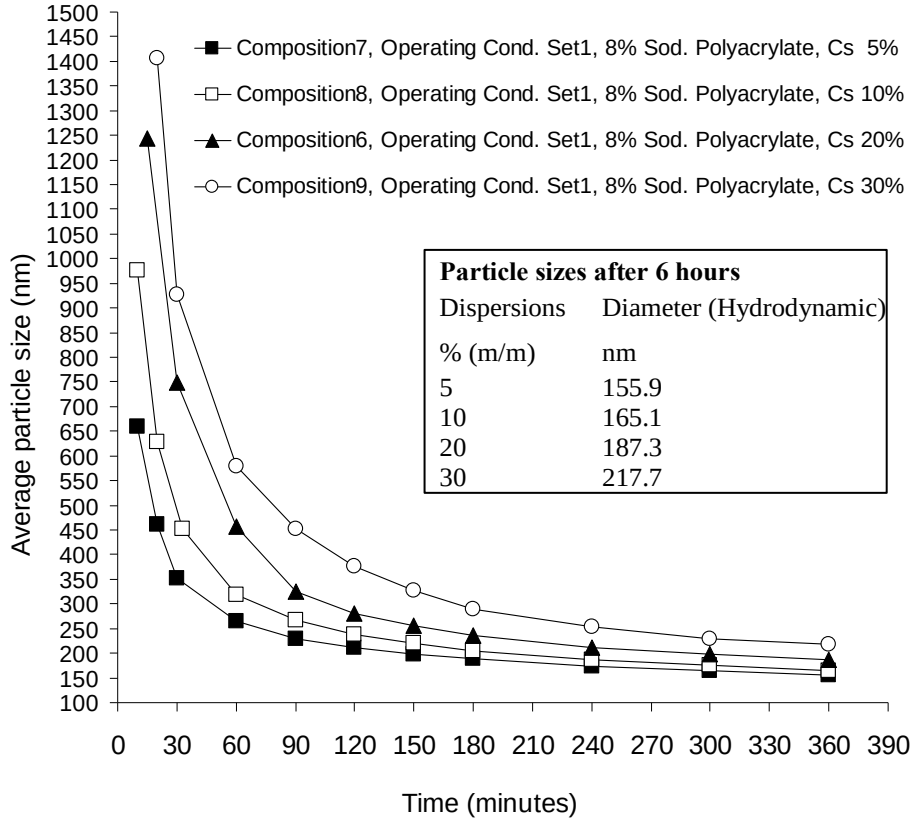

Fig. VI.26: Progression of size reduction process for the composition 7,8,6,9 measured with dynamic light scattering.

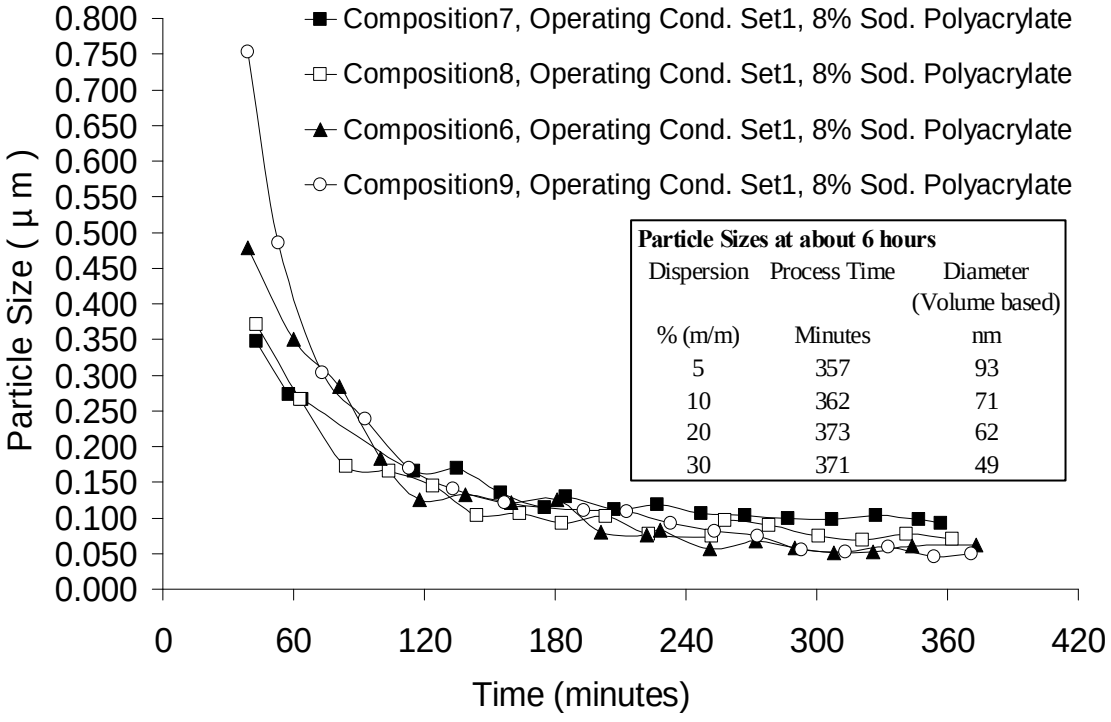

Fig. VI.27: Progression of size reduction process for the composition 7,8,6,9 measured with acoustic attenuation spectroscopy.

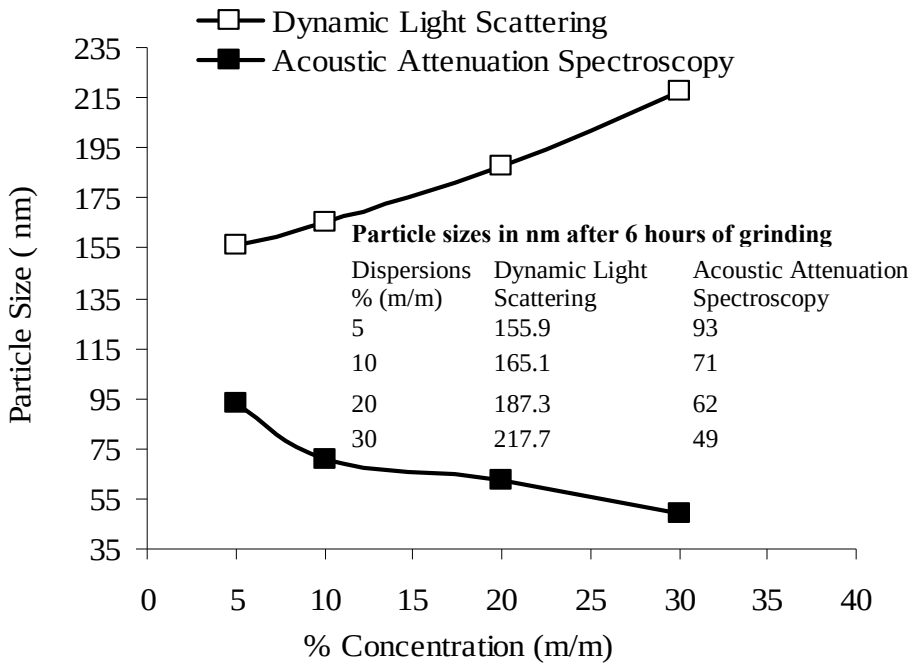

Fig. VI.28: Comparison of results of particle sizes measured with dynamic light scattering and acoustic attenuation spectroscopy.

Our investigation on this problem may be consulted in chapter V. We have discussed three hypotheses in details in order to investigate the problem of particle size measurement:

H1: Different trends are due to different types of diameters of particles measured by two different techniques of particle sizing.

H2: Different trends are due to dilution of samples, in case of particle sizing by dynamic light scattering, which changes the particle size generating misleading information.

H3: The two different trends are due to multiple scattering in acoustic measurements that generates misleading information.

Our investigations reported that because of presence of multiple scattering into the samples the acoustic attenuation spectroscopy shows misleading results. This explains how particle sizing technique may result in wrong interpretation of the product characteristics.

VI.7.4 Operating parameters and product grades

In order to determine the product quality as per definition of quality of ISO 9000:2005 (section VI.2.2), the different product requirements or in other words different product grades must be defined. The products characteristics may be compared with the different grades (different sets of product requirements) in order to determine the product quality. Once grades are defined, it, equally, may be analyzed that the product quality in each grades has been achieved under which conditions of the

operating parameters. Thus a relationship between operating parameters and product quality of different grades may be established. As an example, we defined the following sets of product requirements (product grades). These grades have been developed for explanation purpose only. In commercial production, the users' requirements may serve as a good source of information to develop such grades.

Table VI.11: Different product grades based upon product requirements

Grades	Average particle size (nm)	Stability (zeta potential) mV	Impurity less than: (mg/kg) Zr	Y	Fe	Physical appearance
A1	90-130	Between -30 & -35	15	15	15	No color.
A2	90-130	Between -30 & -35	50	50	50	Little change in color is accepted.
A3	90-130	Between -30 & -35	100	100	100	Little change in color is accepted.
A4	90-130	Between -27 & -29.9	100	100	100	Little change in color is accepted.
A5	131-170	Between -27 & -29.9	15	15	15	No color.
A6	131-170	Between -30 & -38	15	15	15	No color.
A7	171-220	Between -25 & -29.9	15	15	15	No color.
A8	171-220	Between -30 & -38	15	15	15	No color.
A9	221-260	Between -30 & -38	15	15	15	No color.
A10	261-300	Between -27 & -29.9	15	15	15	No color.
A11	261-300	Between -30 & -38	15	15	15	No color.
A12	301-340	Between -25 & -29.9	15	15	15	No color.
A13	301-340	Between -30 & -38	15	15	15	No color.
A14	341-400	Between -27 & -29.9	15	15	15	No color.

The comparison of the product characteristics with the different product grades may establish a relationship between the operating parameters and product quality of a specific grade.

The results of our experiments have been summarized as in table VI.12.

Table VI.12: Relationship between operating parameters and product quality

Grades of product quality	Corresponding operating parameters of the grinding mill		
	Material	Method (Operating conditions)	Measurement (Technique of particle sizing)
A3	Composition 6	Set 2	Dynamic light scattering
A3	Composition 7, 8	Set 1	Dynamic light scattering
A6	Composition 6	Set 1	Dynamic light scattering
A7	Composition 9	Set 1	Dynamic light scattering
A8	Composition 6	Set 1	Dynamic light scattering
A10	Composition 2	Set 1	Dynamic light scattering
A12	Composition 2	Set 2	Dynamic light scattering
A12	Composition 5	Set 1	Dynamic light scattering
A14	Composition 1	Set 1	Dynamic light scattering

Thus, not only the effects of combinations of material, method (set of operating conditions) and measurement technique on product quality may be studied but also the price of the products may be optimized. For example, the table VI.12, explains that product of grade A12, may be produced by two ways: (i) by grinding the dispersion of composition 2 at operating set 2 and (ii) by grinding the dispersion of composition 5 at operating set 1. By costing material, energy, wear and tear in the mill

and loss in grinding media in both cases, the optimum method to produce the product of grade A12 may be identified.

VI.8 Conclusions

Quality is a relative concept. The perception of quality is different in different contexts. Without defining the product requirements, the product quality cannot be determined. Operating parameters such as materials, operating conditions of the mill and measurement techniques influence the product characteristics. The experimental work that takes into consideration the characterization of the operating parameters in a wet grinding process may establish a relationship between the product characteristics and operating parameters. The product whose characteristics are in accordance with a specific product requirement may be regarded as a product of a specific quality. The relationships between (i) operating parameters and product characteristics and (ii) product characteristics and product requirements, provide the insight into the effects of operating parameters on product quality.

The characterization of the materials in this study brings that the dispersions based upon the dispersant sodium polyacrylate are quite suitable in wet grinding process when their proportion is 8% of disperse media. These dispersions show a good stability in terms of zeta potential thought out the grinding process. No aggregation is observed in such dispersions at both set 1 and set 2 of operating conditions. However, the grinding of these dispersions at set 2 creates higher wear and tear in the mill and grinding media. The wear and tear in the mill and grinding media is equally observed in the case of dispersions stabilized with Targon-1128. However, Targon-1128 does not remain efficient in stabilizing the particles in the dispersion after certain grinding hours. In all the compositions of the material based on Targon-1128 an aggregation has been observed. The dispersions prepared with Agnique PG 8107-G are not quite suitable for grinding process because of their inability to create a reasonable stability in particles and problem of foaming. The set 2 as compared to set 1 of operating conditions is helpful in fast size reduction process but the set 2 is disadvantageous in terms of energy consumption. Moreover, the set 2 results in higher wear and tear in the mill and grinding media. The addition of impurities not only affects the colour of the dispersions but also be a factor behind destabilization of the particles.

In particle sizing techniques, acoustic attenuation spectroscopy cannot be considered in the particle sizing of aqueous dispersion of $CaCO_3$ in colloidal range of particle size. The techniques misleads to the results of particle sizes due to multiple scattering.

Pour conclure

La qualité d'un produit est une notion relative et sa perception est différente selon le contexte. Des paramètres tels que les matériaux utilisés, les conditions opératoires et les techniques de caractérisation utilisées influencent les propriétés du produit. Un travail expérimental a été réalisé prenant en considération différents paramètres pour établir une relation entre les caractéristiques du produit obtenu par broyage en voie humide et les paramètres opératoires.

Nous avons observé que contrairement aux autres additifs testés (Targon-1128 et Agnique PG 8107-G), le polyacrylate de sodium (masse molaire 5100) est bien adapté au broyage ultrafin du carbonate de calcium lorsque la concentration est de 8% par rapport à la masse de produit considérée. Le potentiel zeta des particules, mesuré sur des échantillons après différents temps de broyage, suggère que les suspensions restent stables, du point de vue de l'agrégation des fragments produits ; ce qui est confirmé par l'analyse de taille effectuée par diffusion dynamique de la lumière. L'agrégation des fragments n'est pas non plus observée lorsqu'on augmente la vitesse de rotation de l'agitateur mais l'usure des billes de broyage et du revêtement du broyeur est plus importante, en raison de l'accroissement de l'énergie spécifique apportée au système. L'usure des billes et de la chambre de broyage a été observée de manière équivalente lorsque les dispersions sont dispersées à l'aide de Targon-1128 mais la quantité utilisée, bien que importante, ne permet pas de stabiliser les fragments produits au-delà d'un certain temps d'opération et un processus d'agrégation apparaît. L'Agnique PG 8107-G, enfin, s'est avéré ne pas être un additif adéquat pour la dispersion de carbonate de calcium car il ne permet pas d'empêcher l'agrégation des particules fines de carbonate de calcium et provoque la formation de mousse qui perturbe l'opération.

L'étude menée ici en présence de divers additifs, permet de justifier a posteriori l'utilisation du polyacrylate de sodium comme dispersant pour assurer la stabilisation des fragments produits lors du broyage ultrafin en suspension concentrée de carbonate de calcium.

Nous avons également observé que l'utilisation d'une vitesse de rotation du broyeur plus élevée permettait d'atteindre plus rapidement une finesse de produit équivalente à celle obtenue lorsque la vitesse est plus faible mais elle nécessite une énergie spécifique plus importante. Une plus grande vitesse de rotation se traduit aussi par une augmentation de l'usure des billes de broyage et/ou du revêtement de la chambre de broyage ; ce qui nuit également à la qualité du produit. La présence d'impuretés modifie la pureté du produit, sa couleur et peut également être un facteur provoquant la déstabilisation de la suspension.

Enfin, nous pouvons conclure, que lorsque des critères de qualité ont été définis, et moyennant le choix d'une technique de caractérisation adaptée, il est possible de trouver les conditions opératoires permettant d'atteindre le niveau de qualité requis.

VI.9 References

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* *As per requirements of the university, the translation of chapter VI1in French has been provided the end of this chapter.*

VII. Conclusions and Future Work

The particle sizing of dispersions is quite important in the wet grinding process. The information of particle size is required in interpretation, control and optimization of various aspects of the wet grinding process. The particle sizing in a wet grinding process is typical and complex in many senses. There is a need to understand the potentials, limitations and complications of particle sizing techniques in the wet grinding process. This study attempted to address the following problems encountered in the wet grinding process:

- The particle sizing of the dispersions involving impurities and additives.
- The effects of concentrations of the dispersions on particle sizing in the wet grinding process.
- The effects of particle sizing and operating parameters on product quality in the wet grinding process.

In this chapter, we summarize our findings concerning above problems. The issues and aspects that require further attention of the future researcher and scientists have been mentioned in the section of future work.

VII.1 Important conclusions

VII.1.1 Effects of impurities on particle sizing by acoustic attenuation spectroscopy

The first objective of this study was to investigate the effects of impurities on particle sizing by acoustic attenuation spectroscopy with the aim to find the possible ways in which the technique may be applied to wet grinding processes that involve impurities and additives. The lack of understanding (i.e. how and under which conditions to employ the technique when dispersions involve impurities) had halted the application of the technique in many processes such as wet grinding process.

We adopted a comparative approach to investigate the problem. Dispersions of three different concentrations without impurities were characterized by acoustic attenuation spectroscopy. The same dispersions were added with the three types of impurities in four different proportions. We found that all three types of impurities, in all four proportions, affect acoustic attenuation spectrum of the respective dispersion. The interesting finding of our work is that change in acoustic attenuation spectrum because of addition of an impurity, may or may not result in change of original particle size of the disperse medium. Our work brought out the conditions in which it is possible to predict the

conditions (i- concentration of dispersion; ii - proportion of impurity) at which the particle (or aggregate) size of the disperse medium is not influenced by the addition of the impurity. In such cases, we can calculate the acoustic contribution of the impurity in the total acoustic attenuation spectrum of the dispersion. This contribution may be subtracted from the total attenuation spectrum of the dispersion in order to get more realistic information of the particle size of the disperse medium. The approach opens a way to study dispersions with impurities using acoustic attenuation spectroscopy.

The cases in which the size of the disperse medium seems to be influenced by the addition of certain quantities of impurities may be explained based on the existence of multiple scattering (a complex phenomenon that disturbs attenuation in acoustic measurement), interaction between particles of the disperse medium or interaction between particles of the impurity and those of the disperse medium. In such cases, it becomes more difficult to get exact particle size information of the disperse medium by using acoustic attenuation spectroscopy. In the study, higher quantities of impurities were considered in order to emphasize their effect on acoustic response. However, under usual conditions, when the proportion of an impurity is less than 20% of the weight of the disperse medium, it may be assumed that presence of the impurities in a dispersion may lead to predictable effects, except for the impurities (such as sodium polyacrylate) that may influence electrostatic and steric stabilization of the dispersions.

VII.1.2 Effects of concentrations of the dispersions on particle sizing

The second objective of the study was to investigate how different concentrations of a dispersion influence particle sizing during production of fine particles in wet grinding process carried out by means of a stirred media mill. Especially, we aimed to compare the results of particle sizing of different techniques with the goal to find the reasons of differences in the results obtained through different techniques.

Our investigations brings that the concentration of the dispersion plays an important role in particle sizing in size reduction process. This role emerges very distinctively when particles enter from micron to fine particle size range during stirred media milling. Acoustic attenuation spectroscopy, which is generally considered to be capable of measuring average particle size of the dispersions at different values of concentrations, shows certain limitations in stirred media milling. The technique explains that use of relatively concentrated dispersions may be favorable in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters. However, dynamic light scattering demonstrates that use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling. Our investigations bring out three important results:

- The opposite trends are not because of different types of diameters considered in acoustic attenuation spectroscopy and dynamic light scattering.

- It is not the dilution process in case of dynamic light scattering that resulted in misleading information by changing the particle size because of aggregation or de-aggregation etc.
- It was determined that in particle sizing by acoustic attenuation spectroscopy during wet grinding process, an attenuated acoustic wave from one particle is scattered by other particles changing the acoustic signals and thus bringing to misleading results. The phenomenon is called multiple scattering.

The study demonstrated that particle sizing by acoustic attenuation spectroscopy cannot be considered valid at higher concentration of samples of dispersions during stirred media milling because of multiple scattering that influence the results. If concentration of the sample of dispersions is reduced considerably in particle sizing by means of acoustic attenuation spectroscopy in stirred media milling, then anomalies in the results may be avoided. In such cases both the techniques shows reasonable agreement that use of relatively dilute dispersions favors in achievement of finer particles during stirred media milling carried out under a set of fixed operating parameters.

VII.1.3 Effects of particle sizing and operating parameters on product quality

As an extension of the previous work, the third objective of the study was to analyze the effects of three important parameters (i.e., materials, methods and measurements) on product quality in the wet grinding process.

A wet grinding process may involve different sorts of measurements such as flow rate, energy, pH etc. The particle sizing is one of the most important measurements in a grinding process and it is therefore, it had been focused in the previous chapters of this manuscript.

Quality is a relative concept. The perception of quality is different in different applications. This study proposes a method of measuring the effects of operating parameters on product quality based on definition of quality as in ISO 9000:2005. We present the idea that by measuring the product characteristics against operating parameters and then comparing the product characteristics against selected product requirements (grades), a relationship between operating parameters and product quality may be established.

Our work confirms that operating parameters such as materials, operating conditions of the mill and measurement techniques influence the product characteristic. The characterization of the materials brings that the dispersions based upon the dispersant sodium polyacrylate are highly suitable in the grinding process when their proportion is 8% of disperse media. These dispersions show a reasonable good stability in terms of zeta potential through out the grinding process. No aggregation is observed at both set 1 and set 2 of operating conditions. However, the grinding of these dispersions at set 2 (i.e. at higher grinding speed) creates higher wear and tear in the mill and grinding media. The wear and

tear in the mill and grinding media is equally observed in the case of dispersions stabilized with Targon-1128. However, Targon-1128 does not remain efficient in stabilizing the particles in the dispersion after certain grinding hours even if it is used in higher proportion of 8%. In all the compositions of the material based on Targon-1128 an aggregation has been observed. The dispersions prepared with Agnique PG 8107-G are not quite suitable for grinding process because of their inability to create a reasonable stability in particles and problem of foaming.

The set 2 (higher grinding speed) as compared to set 1 (lower grinding speed) is helpful in carrying a rapid size reduction process but it must be noted that set 2 causes higher wear and tear in the mill and grinding media. The impurities, produced by wear and tear of the mill and grinding media, affect the color of the dispersions. In addition, they may influence stabilization and other characteristics of the dispersions.

In particle sizing techniques, acoustic attenuation spectroscopy cannot be considered in the particle sizing of aqueous dispersion of $CaCO_3$ especially in colloidal range of particle size. The techniques may mislead in interpretation of the product characteristic and hence may influence the measurement of product quality.

VII.2 Future work

This section presents the issues and the technical problems that may be undertaken by the future researcher for research and development purpose.

- Our work on effects of impurities on particle sizing by acoustic attenuation spectroscopy divided the impurities into two groups: (i) with predictable effects (ii) with in-predictable effects. Our work explained how we can determine the conditions of (i- concentration of dispersion; ii - proportion of impurity) in which an impurity will fall into group of predictable effects. In such case, we proposed a method to subtract the acoustic contribution of the impurity from the total acoustic attenuation in order to get the exact acoustic contribution of the dispersion. However, we had not much success to understand the situation in which an impurity is under “in-predictable effects”.

  In a series of experiments, we prepared different combinations of dispersions with impurities (group of un-predictable effects) and tried to analyze the matter by means of image analysis technique. However, we had not been able to extract sound and meaningful information. This remains an open issue and may be focused by the future researchers.

- In our work on effects of impurities on particle sizing by acoustic attenuation spectroscopy, we brought the conditions in which it is possible to predict the conditions (i- concentration of dispersion; ii - proportion of impurity or another phase) at which the particle (or aggregate) size of the disperse medium is not influenced by the addition of the impurity or another phase. In such

case, we can divide the total acoustic attenuation spectrum in: (i) acoustic spectrum of pure dispersion (ii) acoustic spectrum of impurity (or another phase). The adequate developments in software of the acoustic attenuation spectrometer may permit in studying exact particles size information of pure dispersion as well particle sizes of different phases of the dispersions. This could be particularly interesting in specific industrial applications where product, impurities or other phases in the dispersions are already well defined. The researchers or the computer engineers in the future may address this matter. Similarly, another interesting work is of development of the data base that may list the impurities, their proportions and effects on acoustic attenuation.

- Our investigations on effects of concentration of the dispersion on particle sizing during wet grinding process highlighted the problem of multiple scattering. Under such conditions, the ECAH theory, on which acoustic attenuation spectroscopy lies, does not remain valid. In order to control various aspects of particle sizes of different particulate system especially of fine and nano particles, it is imperative to develop new theories that successfully may take into consideration the matter of multiple scattering.

- Ishikawa (1990) pointed out six important parameters (i.e. material, machine, method, measurement, manpower and management) that may influence quality in production of a product. In this study, we have focused on some aspects of material (different compositions), method (two operating sets) and measurement (of particle sizing). Different aspects of grinding machine (mill) such as design and geometry have not been considered by us in the study. In the future, it may be interesting to analyze the effects of different types of mills (such as disc mill, pin mills and annular gap mills) on product quality.

- In our work, we tested three dispersing agents. We reported how they affect product quality without going into details of their stabilizing mechanism. The future researcher may undertake the effects of such dispersing agents on product quality by focusing on the mechanism of stability. In this regard, the use of the techniques that permit determining the shape of particles (or aggregates) and manner of attaching or binding with additives may be informative.

VII Conclusions et Perspectives

La caractérisation de la taille des particules est une donnée essentielle dans les procédés de broyage en voie humide. L'information relative à la taille est nécessaire pour l'interprétation des données, le contrôle et l'optimisation des procédés selon divers aspects. La caractérisation de taille au cours de procédés de broyage en voie humide est spécifique et complexe pour différentes raisons. Il est nécessaire de mieux connaître les potentialités, les limitations et les contraintes induites par les techniques de caractérisation de taille sur ces procédés. Cette étude avait pour objectifs de répondre aux problèmes suivants rencontrés dans les procédés de broyage en voie humide :

- la caractérisation de la taille de particules dans des dispersions concentrées contenant des impuretés ou des additifs
- la connaissance de l'effet de la concentration en solide sur la taille des particules dans les procédés de broyage en voie humide
- la connaissance des effets de la caractérisation de taille et des paramètres opératoires sur la qualité des produits formulés par broyage en voie humide.

Nous résumons ici les principaux résultats de notre travail relatifs à ces différentes questions. Les aspects qui nécessiteraient des développements futurs sont mentionnés en perspectives.

VII.1 Principales conclusions

VII.1.1 Effet des impuretés sur la caractérisation par spectroscopie acoustique

Le premier objectif de l'étude était d'analyser les effets des impuretés sur la mesure de taille par spectroscopie acoustique dans le but de trouver les conditions d'utilisation de cette technique pour le suivi de taille dans des procédés de broyage en voie humide. Dans ces procédés, les suspensions traitées contiennent généralement des impuretés et/ou des additifs et le manque d'informations (c'est-à-dire comment et sous quelles conditions utiliser la technique acoustique lorsque les dispersions contiennent des impuretés) a quasiment arrêté l'utilisation de cette technique dans de nombreux procédés (tels que les procédés de broyage par microbilles).

Nous avons mené une étude comparative pour analyser ce problème. Des dispersions de différentes

concentrations sans impureté ont été analysées par spectroscopie acoustique. Puis nous avons analysé les mêmes dispersions dans lesquelles nous avions ajouté des impuretés de différentes natures et concentrations. Nous avons observé que quelles que soient la nature et la quantité d'impuretés, les spectres d'atténuation acoustiques étaient modifiés. Un résultat intéressant est que le changement dans le spectre d'atténuation du fait de l'ajout d'une impureté, peut ou ne pas engendrer une modification de la taille originale des particules dans la dispersion. Nous avons déterminé les situations pour lesquelles il est possible de prédire les conditions, c'est-à-dire la concentration de la dispersion et la proportion en impureté, auxquelles la taille des particules (ou des agrégats) n'est pas influencée par l'ajout de l'impureté. Dans ces situations nous pouvons calculer la contribution de l'impureté sur la réponse acoustique globale. Cette contribution spécifique peut alors être déduite pour obtenir une information plus précise sur la distribution de taille du produit en suspension. Si la nature et la concentration de l'impureté sont connues, l'approche proposée permet l'étude de dispersions contenant des impuretés par spectroscopie acoustique.

Dans les cas où la taille du milieu dispersé semble influencée par l'addition de certaines quantités d'impureté, la réponse acoustique peut être expliquée en se basant sur l'existence d'un phénomène de diffusion acoustique multiple ou par une modification des propriétés interactives entre les particules ou encore entre les particules du milieu dispersé et celles de l'impureté.

VII.1.2 Effet de la concentration en solide lors de la caractérisation de taille de particules

Le second objectif de cette étude était d'analyser comment la concentration d'une dispersion pouvait influencer la mesure de la taille de particules lors d'un procédé de broyage en voie humide mené à l'aide d'un broyeur à billes agité. Plus particulièrement, nous souhaitions comparer les résultats de l'analyse de taille obtenue avec différentes techniques et de comprendre les raisons des différences observées.

Nos recherches ont montré que la concentration en solide joue un rôle prépondérant dans la caractérisation de taille associée au procédé de réduction de taille. Cette implication apparaît de manière cruciale quand la taille des particules passe du domaine micronique au domaine submicronique au cours du broyage dans un broyeur à microbilles. La spectroscopie acoustique, qui est généralement considérée comme une technique apte à mesurer la taille des particules dans des dispersions quelle que soit leur concentration, a montré quelques limitations lors de son utilisation pour le suivi de ce type de procédé. Cette technique suggèrerait que l'emploi de dispersions relativement concentrées serait favorable à l'obtention de très fines particules au cours du broyage en voie humide dans un broyeur à billes agité (les autres conditions opératoires étant fixées). Au contraire, les analyses par diffusion dynamique de la lumière montrent que l'utilisation de dispersions

peu concentrées serait plus favorable pour obtenir de très fines particules. Nous avons pu établir que :

- les tendances inverses ne sont pas dues au fait que les techniques acoustique et par DLS mesurent physiquement des grandeurs différentes,
- ce n'est pas l'étape de dilution nécessaire lorsque les analyses sont effectuées par DLS qui changerait la taille des particules par des processus d'agrégation ou de de-agrégation
- lors de la caractérisation par spectroscopie acoustique, l'onde secondaire générée par une particule au passage de l'onde acoustique est perturbée par la présence des autres particules, ce qui a pour effet de modifier la réponse acoustique du système et de conduire à des résultats erronés. Ce phénomène est connu sous le nom de diffusion multiple.

Nous avons montré que la mesure de taille par spectroscopie acoustique ne peut pas être considérée comme correcte pour des suspensions très concentrées traitées par broyage humide dans un broyeur à billes agité en raison des phénomènes de diffusion multiple qui faussent les résultats. Si la concentration des échantillons de dispersions est abaissée, alors les analyses par spectroscopie acoustique ne font plus apparaître de telles anomalies et les deux techniques analytiques testées montrent des similitudes de comportement quand à l'effet de la concentration en solide sur le résultat d'une opération de broyage par microbilles conduite sous des conditions opératoires fixées.

VII.1.3 Effet de la caractérisation de taille et d'autres paramètres sur la qualité du produit

Par extension des travaux précédents, le troisième objectif de la thèse était d'analyser les effets de trois paramètres importants, en relation avec le matériau, les conditions de fonctionnement du broyeur et les techniques d'analyse, sur la qualité du produit obtenu par broyage en voie humide. La mesure de la distribution de taille du produit est une donnée essentielle dans les procédés de broyage et elle a donc été tout particulièrement étudiée dans les premières parties de la thèse.

La qualité est un concept relatif. La perception de la qualité est différente selon les applications. Dans ce travail, nous avons adopté une démarche pour mesurer les effets de différents paramètres sur les caractéristiques du produit broyé en se basant sur une définition de la qualité telle que dans la norme ISO 9000 :2005. Nous avons montré qu'en mesurant les propriétés du produit en fonction des paramètres opératoires et en confrontant ensuite ces propriétés avec des critères de qualité fixés, nous pouvions établir une relation entre les paramètres opératoires et la qualité du produit.

Ce travail a également montré que plusieurs paramètres relatifs au matériau, aux conditions de fonctionnement et aux techniques de mesure pouvaient influencer les caractéristiques du produit. Nous avons observé que les suspensions de carbonate de calcium dispersées à l'aide de polyacrylate de

sodium avec une concentration de 8% (par rapport à la masse de solide) se comportaient de manière tout à fait correcte lors du broyage. Les suspensions broyées semblent stables si on se réfère aux valeurs du potentiel zeta des particules en suspension et les courbes granulométriques ne mettent pas en évidence de processus de re-agrégation des fines produites au cours du procédé. Différentes conditions de fonctionnement du broyeur peuvent être appliquées, mais certaines conditions, comme une vitesse de rotation de l'agitateur plus élevée, créent une usure des billes et du revêtement du broyeur plus importante. Les phénomènes d'usure ont aussi été observés lorsqu'on utilise d'autres agents dispersants comme le Targon-1128. Cet additif, même utilisé en proportion relativement importante, s'est en plus avéré insatisfaisant pour assurer la stabilisation des particules de carbonate de calcium après plusieurs heures de fonctionnement discontinu. Les analyses faites sur toutes les dispersions contenant du Targon-1128 montrent la présence d'agrégats. Enfin, les dispersions préparées en utilisant de l'Agnique 8107-G ne permettent pas un fonctionnement correct du procédé, car cet agent ne permet pas de stabiliser les particules et entraîne la formation de mousse. Il est à noter que les impuretés contaminant le produit affectent non seulement la pureté et la couleur mais qu'elles peuvent aussi favoriser la déstabilisation des suspensions. Pour tous les essais réalisés, l'augmentation de la vitesse de rotation de l'agitateur se traduit par une accélération du processus de réduction de taille mais une augmentation de l'énergie spécifique utilisée.

Enfin, comme nous l'avions évoqué précédemment, la technique de mesure utilisée peut aussi avoir un impact sur la qualité du produit. En particulier, la spectroscopie acoustique utilisée dans le cadre de ce travail s'est avérée insatisfaisante pour mesurer en ligne la distribution de taille du produit broyé dès lors que celui-ci atteint des dimensions submicroniques.

VII.2 Perspectives

Cette section présente les perspectives et les problématiques qui nécessiteraient des développements futurs :

- L'analyse que nous avons menée sur l'effet des impuretés sur la caractérisation de taille par spectroscopie acoustique a conduit à la définition de deux groupes : les impuretés qui ont un effet prévisible et celles qui ont un effet imprévisible. Nous avons montré comment on peut déterminer les conditions pour lesquelles la taille des particules (ou agrégats) du milieu dispersé n'était pas influencée par la présence de l'impureté, lorsqu'il s'agissait d'impuretés dont les effets étaient prévisibles. Dans ces situations, on peut calculer la contribution de l'impureté sur la réponse acoustique. Nous avons proposé alors de la soustraire du spectre global pour avoir une information plus précise sur la distribution de taille des particules du produit d'intérêt. Cependant, nous ne savons pas comment traiter l'information sur la réponse acoustique lorsqu'il s'agit d'impuretés dont les effets sont imprévisibles.

Lors d'une série d'expériences, nous avons préparé différentes dispersions contenant des impuretés ayant un effet imprévisible et nous avons tenté d'examiner une telle situation par analyse d'image. Cependant, nous ne sommes pas parvenus à un résultat tangible. Cette problématique pourrait être approfondie dans des travaux futurs.

- Par ailleurs, lorsque les impuretés sont inertes vis-à-vis du produit, notre étude a montré que le spectre d'atténuation pouvait être considéré comme résultant de deux contributions : le spectre d'atténuation dû à la présence des particules de la dispersion et le spectre d'atténuation dû à la présence de l'impureté. Or, quand le milieu dispersé contient deux ou plusieurs constituants sous forme dispersée, il serait intéressant de pouvoir obtenir la distribution de taille de chaque constituant. Toutefois, l'analyse de milieux contenant plusieurs constituants nécessiterait le développement des logiciels existant actuellement. Cela aurait un intérêt dans des applications industrielles particulières, lorsque le produit d'intérêt, les impuretés ou les différents constituants sont déjà connus. Des développements futurs pourraient être entrepris dans cette direction. Une autre voie intéressante serait le développement d'une base de données qui pourrait lister les impuretés, leurs proportions et leurs effets sur la réponse acoustique lorsqu'elles ne modifient pas la distribution de taille du produit.
- Nos travaux sur les effets de la concentration en solide sur la caractérisation de la taille en ligne d'un procédé de broyage par spectroscopie acoustique ont mis en évidence le problème de la diffusion acoustique multiple. Dans de telles situations, la théorie ECAH, qui est à la base de l'interprétation des spectres d'atténuation acoustique, est insuffisante. Afin de maîtriser divers aspects en relation avec la taille des particules dans les procédés particulaires, spécialement pour les procédés mettant en œuvre des particules ultrafines ou des nanoparticules, il est impératif de développer de nouvelles théories qui prennent en considération les effets de diffusion multiple.
- Ishikawa (1990) a identifié six paramètres importants qui peuvent influencer la qualité d'un produit (le matériau, l'appareil, la méthode, les techniques de mesure, l'opérateur et le management). Dans notre étude sur la qualité du produit, nous avons considéré les effets de quelques paramètres comme la nature et la quantité d'additifs, les techniques de caractérisation de la taille et la vitesse de rotation de l'agitateur. Nous n'avons pas considéré d'autres paramètres comme les différentes géométries de broyeur à billes sur la qualité du produit. Il pourrait être intéressant d'effectuer ce type d'analyse. Par exemple, on pourrait analyser les effets sur la qualité du produit engendrés par la forme de l'agitateur qui, comme nous l'avons évoqué dans le chapitre II, peuvent être sous forme de disques, de doigts ou de forme annulaire.

- Dans ce travail, nous avons considéré en particulier trois additifs particuliers. Nous avons montré comment ils affectent la qualité du produit sans analyser de manière plus approfondie le mécanisme de stabilisation. Des recherches futures pourraient être effectuées dans ce sens, c'est-à-dire sur l'influence de différents types d'additifs en se focalisant sur les mécanismes de stabilisation mis en œuvre. En particulier, il est important de comprendre pourquoi un dispersant qui permet de stabiliser les dispersions au début du procédé de broyage, ne permet pas après un certain temps d'opération d'assurer une stabilisation suffisante pour empêcher l'agrégation des particules. L'utilisation d'autres techniques analytiques, qui permettrait de renseigner sur la forme ou la structure des agrégats ou encore sur l'adhésion des additifs sur les particules de carbonate de calcium, serait probablement très enrichissante.

About the author

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Muhammad Asif INAM

PERSONAL INFORMATION

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EDUCATION AND QUALIFICATION

PhD Process Engineering: From " Institut National Polytechnique de Toulouse", University of Toulouse, France. **(2010)**

M.S. Management Science: From "Karachi Institute of Economics & Technology" Pakistan. *Specialization: Engineering Management* **(2005)**

B.Sc. Chemical Engineering: From "Institute of Chemical Engineering & Technology", University of the Punjab, Pakistan. **(2001)**

PROFESSIONAL POSITIONS

Dec. 2006 - present: Researcher (PhD student) in "Laboratoire de Génie Chimique" Toulouse, France. **3.5 years**

Nov. 2001- June 2006: Engineer / Assistant Manager in "Pakistan Space & Upper Atmosphere Research Commission (SUPARCO)" in R&D projects for production of different polymeric products. **4.7 years**

PAPERS, POSTERS AND CONFERENCES

Papers:

- Effects of impurities on particle sizing by acoustic attenuation spectroscopy. ***(Reference: Powder Technology 201 (2010) 21–26)***
- Effects of concentration of dispersions on particle sizing during production of fine particles in wet grinding process ***(Accepted for publication in the journal of Powder Technology)***

Conferences and Posters:

- Oral presentation in "The World Congress on Particle Technology" on "Effects of operating parameters on product quality in stirred media mills for production of nanoparticles" in Nuremberg, Germany (26-29 April 2010).
- Oral and poster presentation on "Effects of concentration of dispersions on particle size in wet grinding process for production of nanoparticles" in the national conference "Science et technologie des poudres & matériaux frittés" Montpellier, France.
- Oral and poster presentation on "LASER Techniques" in a conference organized by "Ecole doctorale MEGEP" Toulouse, France.

RESEARCH INTERESTS

- Characterization of the dispersions of fine and nano particles.
- Surface and interface engineering of the particles.
- Particle sizing, steric and electrostatic stabilization of the particles.
- Particle dispositions on surfaces.
- Dry and wet grinding processes.

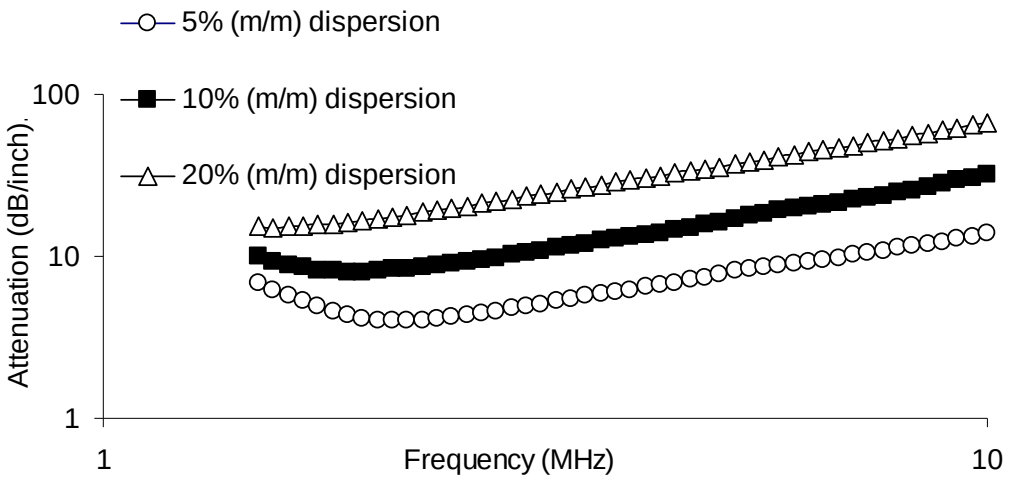
CAREER INTERESTS

- Research
- Teaching / Lectureship
- Project management
- Product development
- Production management
- Quality management

LANGUAGE SKILLS

English:	Fluent (Read, write, speak, listen)
French:	Average (Read, write, speak, listen)
Urdu:	Fluent (Read, write, speak, listen)
Punjabi:	Fluent (Read, write, speak, listen)

Appendix A



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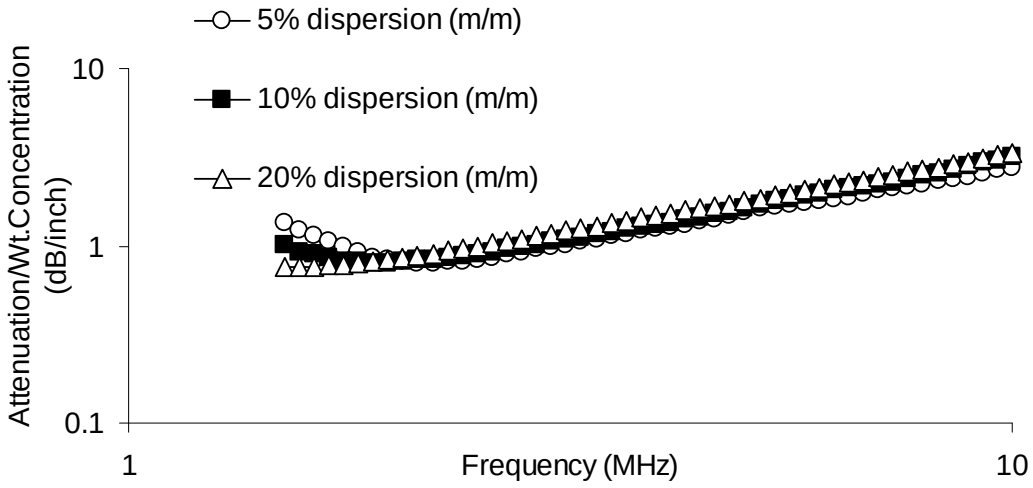
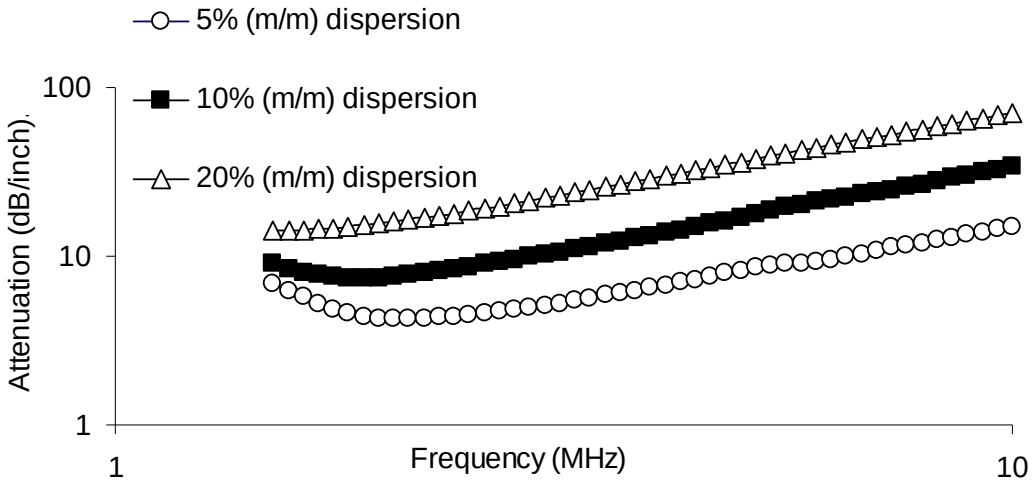


Fig. A. 1(b)

Fig. A. 1: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 5% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 5% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity.



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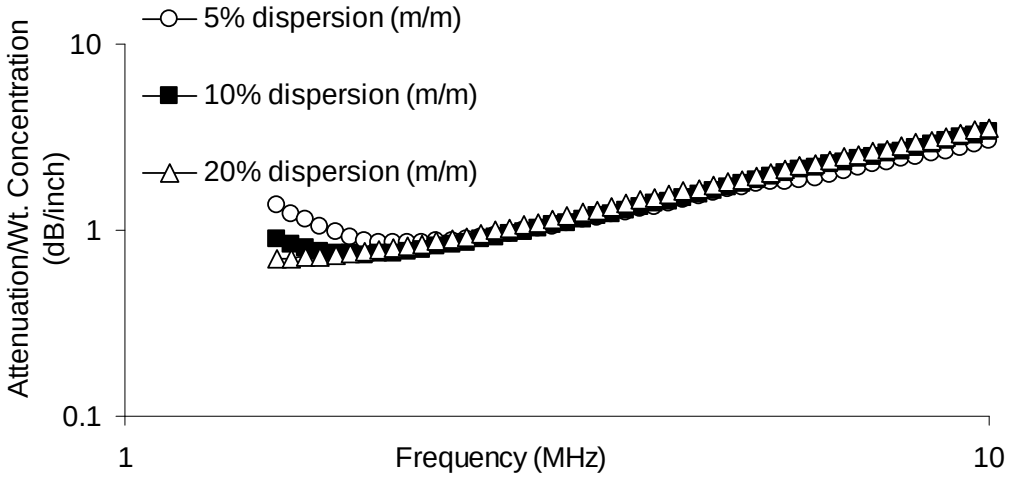
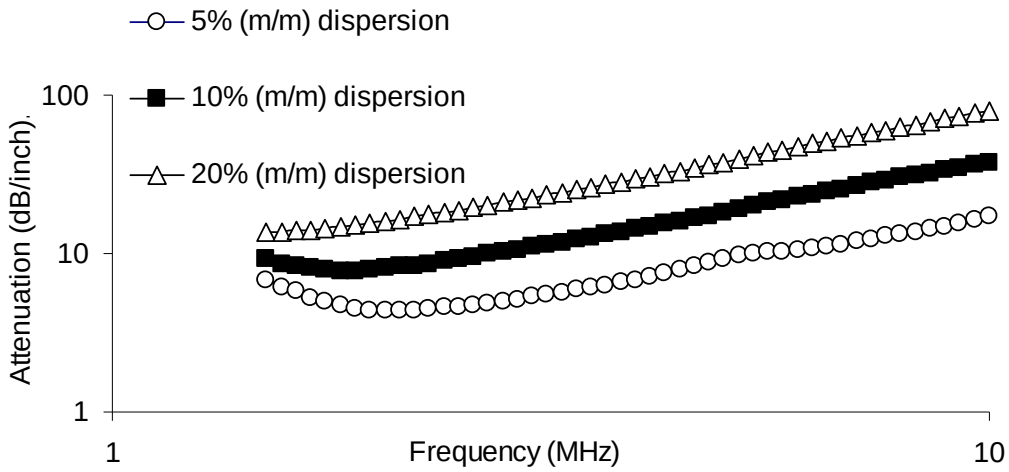


Fig. A. 2(b)

Fig. A. 2: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 10% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 10% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity.



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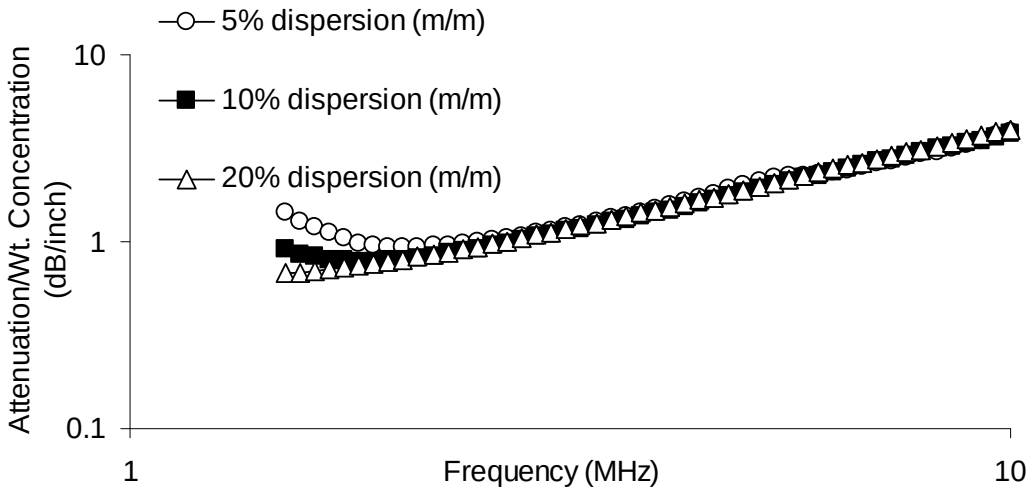
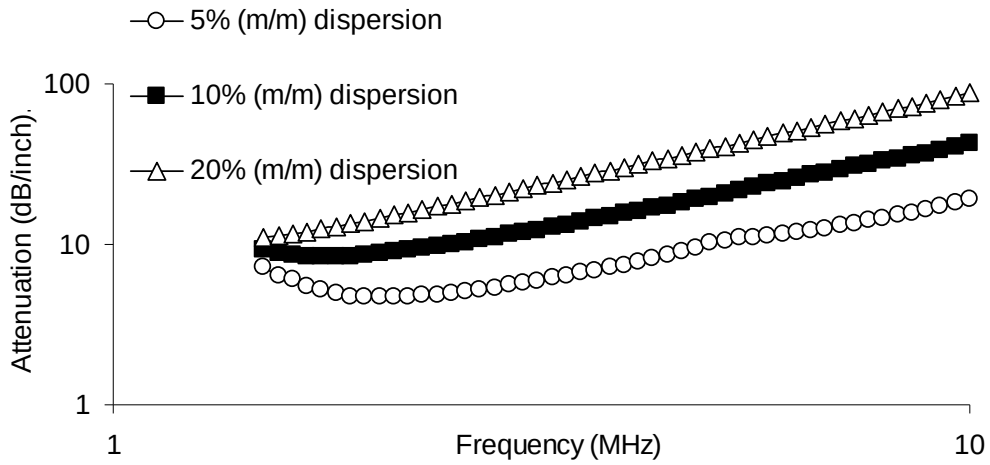


Fig. A. 3(b)

Fig. A. 3: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 20% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 20% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity.



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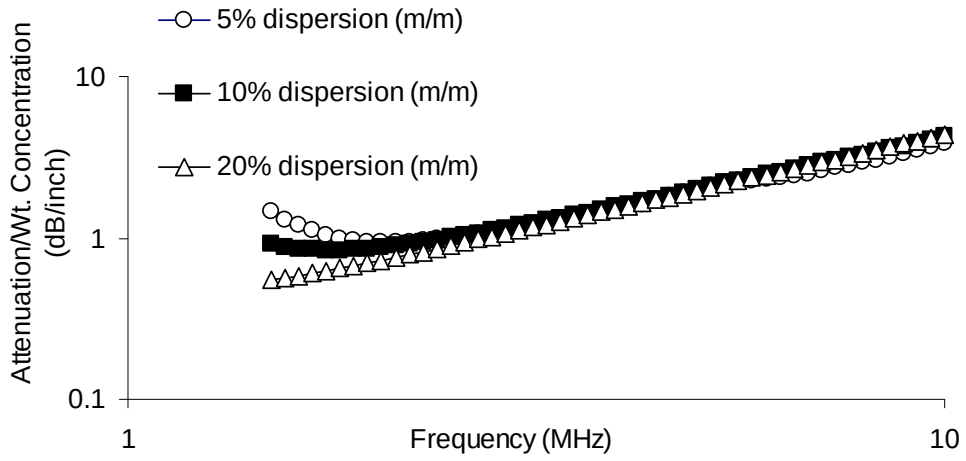
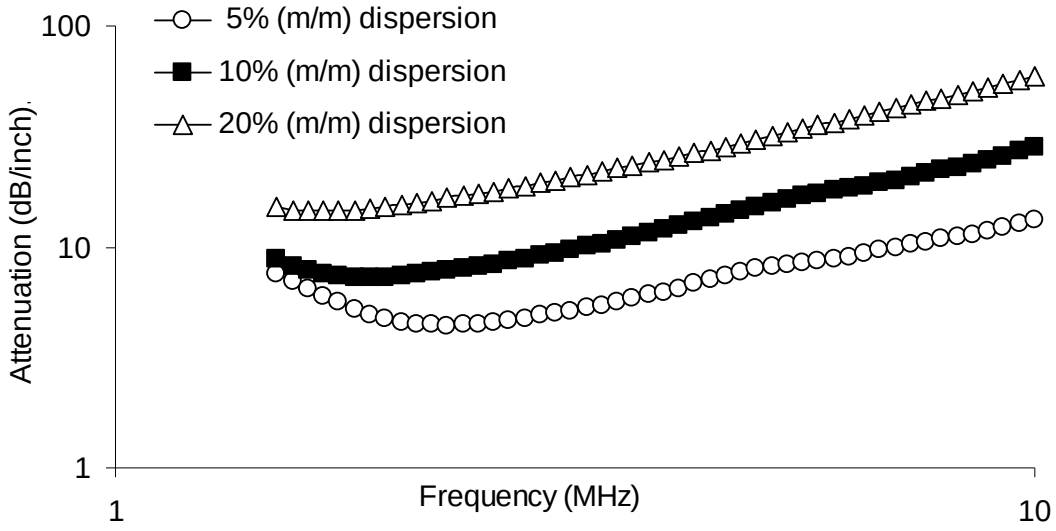


Fig. A. 4(b)

Fig. A. 4: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 30% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 30% $MgCO_3$ of the weight of $CaCO_3$ is present as impurity.



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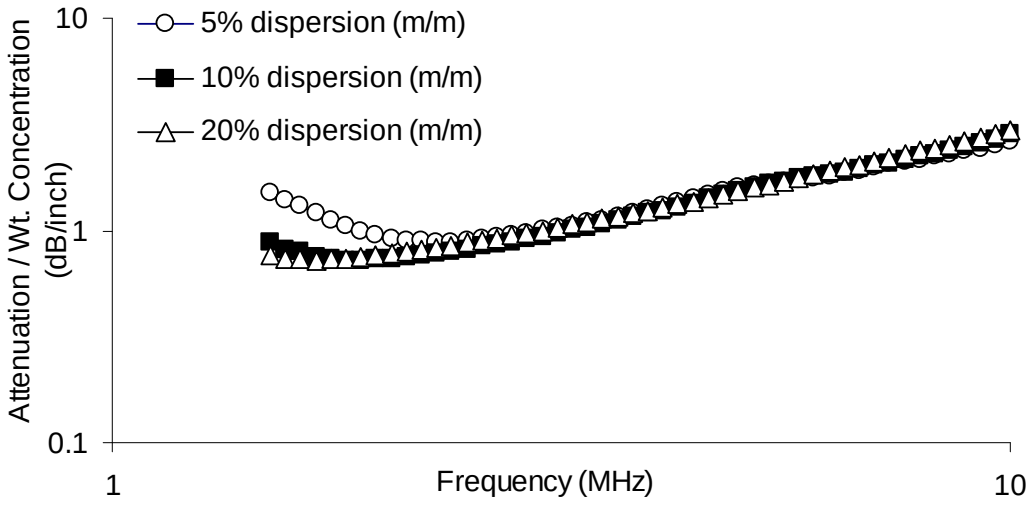
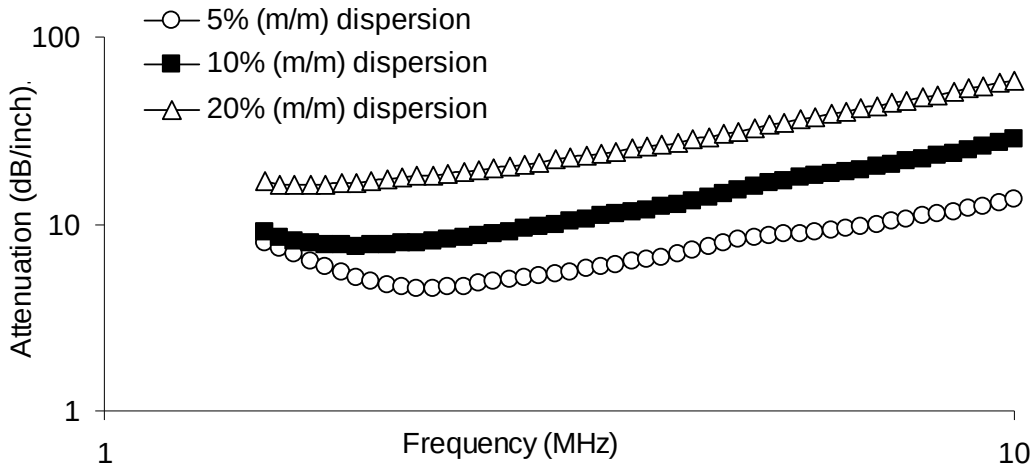


Fig. A. 5(b)

Fig. A. 5: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 5% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 5% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity.



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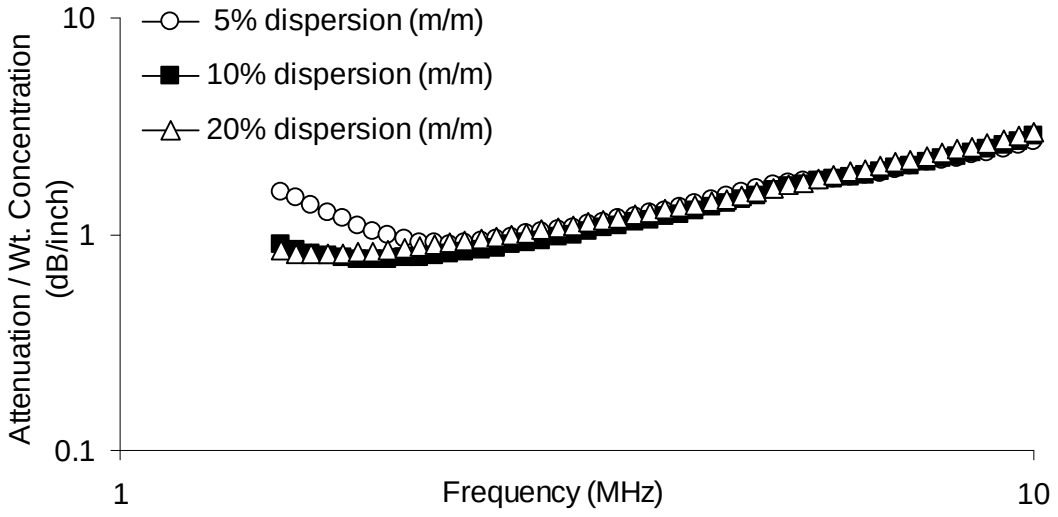


Fig. A. 6(b)

Fig. A. 6: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 10% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 10% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity.

Appendix B

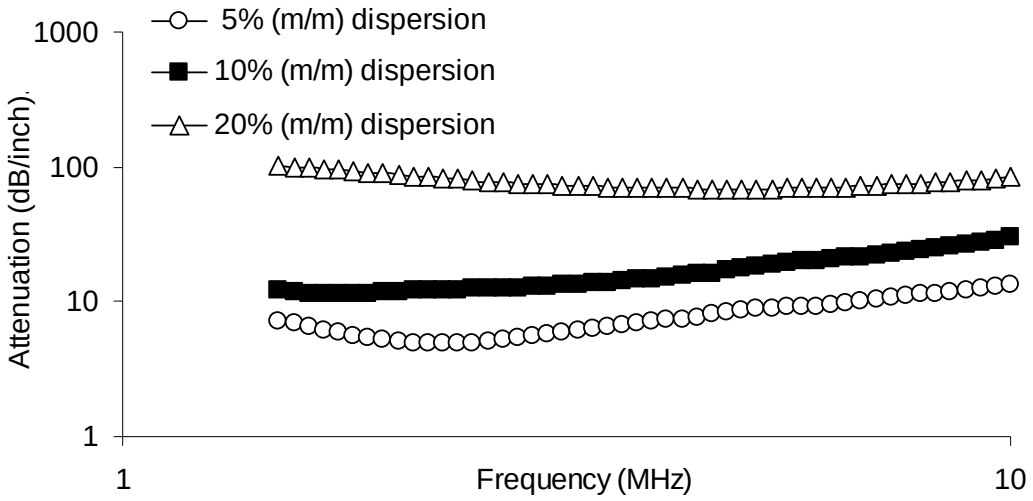


Fig. B. 1(a)

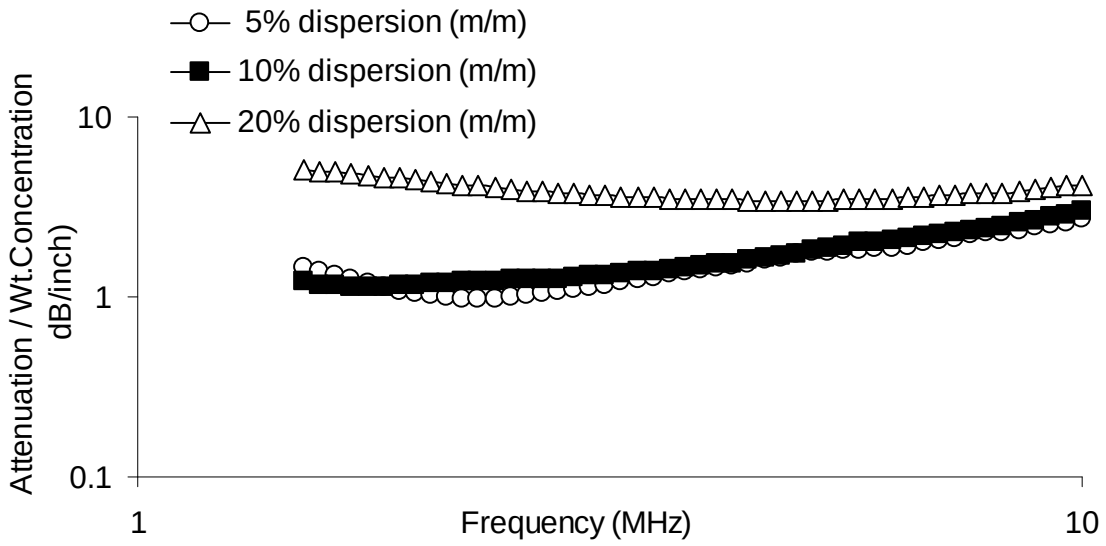
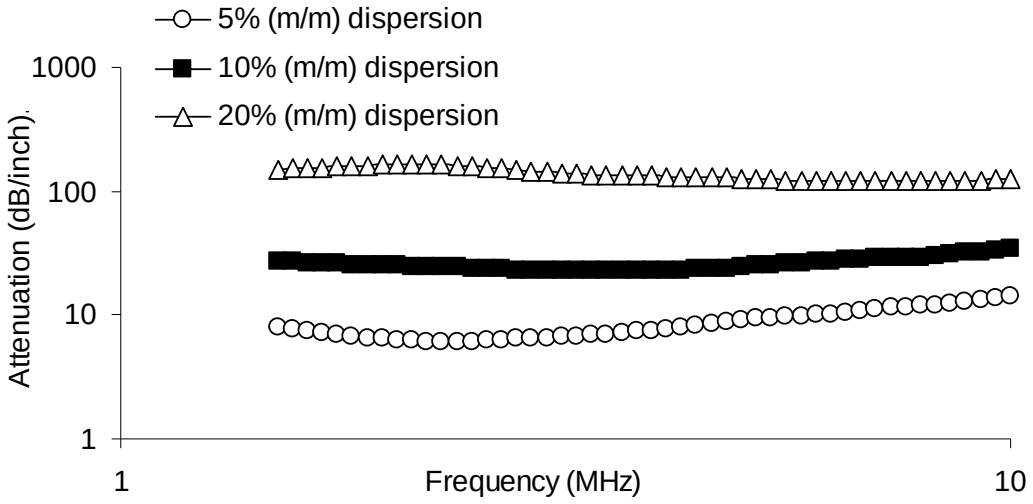


Fig. B. 1(b)

Fig. B. 1: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 20% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 20% $NaNO_3$ of the weight of $CaCO_3$ is present as impurity.



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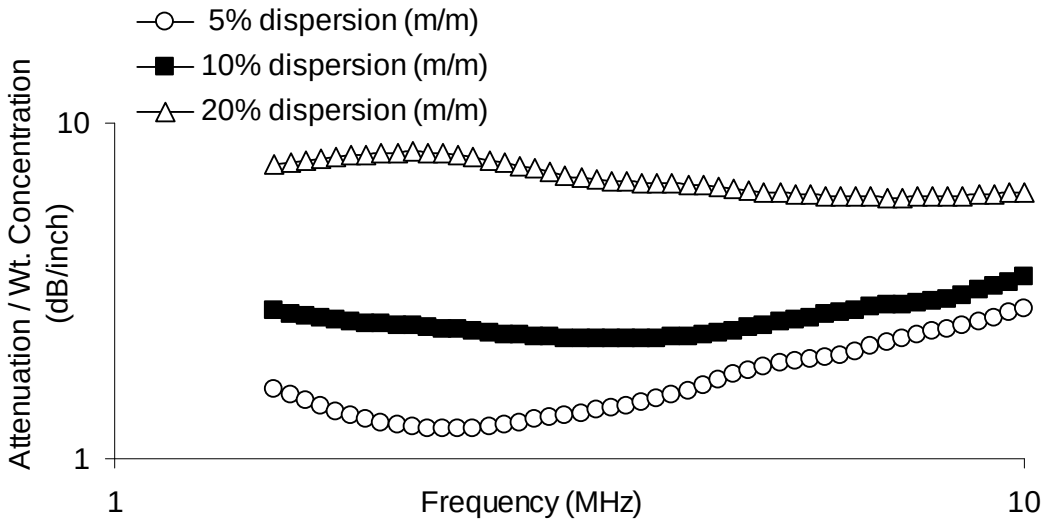
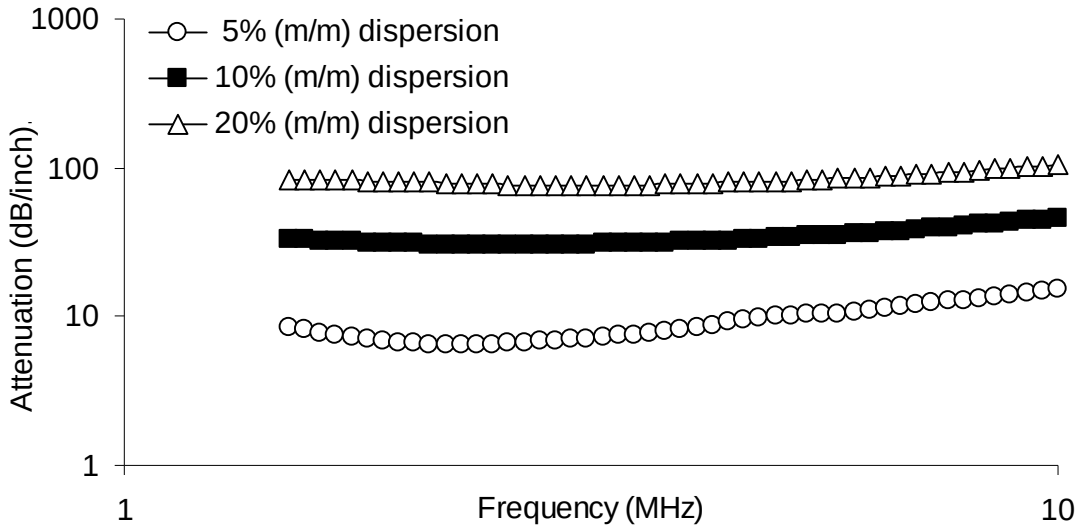


Fig. B. 2(b)

Fig. B. 2: (a) Acoustic attenuation spectra of dispersions of CaCO3 at different concentrations. In each case, 30% NaNO3 of the weight of CaCO3 is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of CaCO3 at different concentrations. In each case, 30% NaNO3 of the weight of CaCO3 is present as impurity



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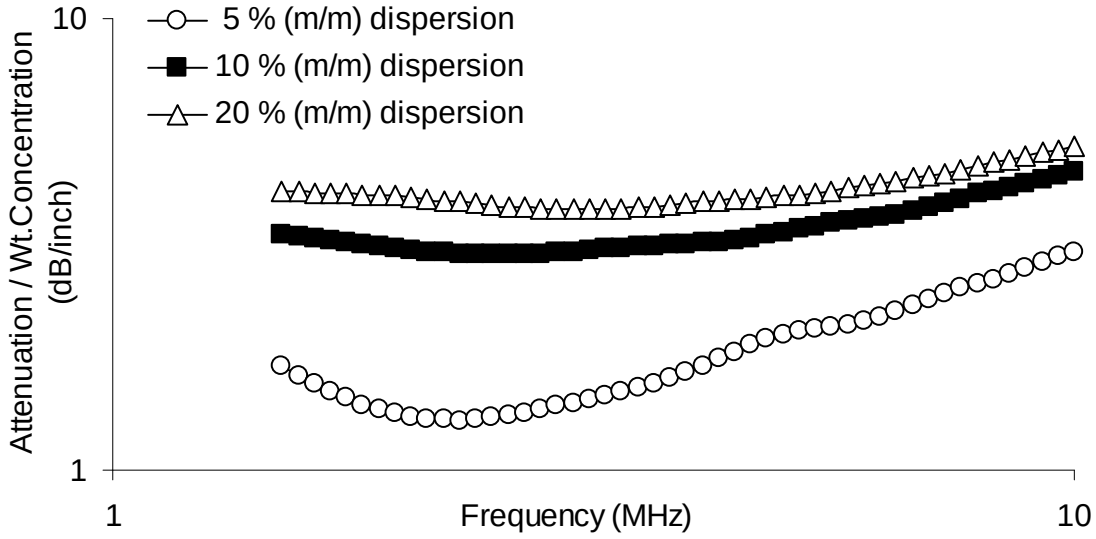
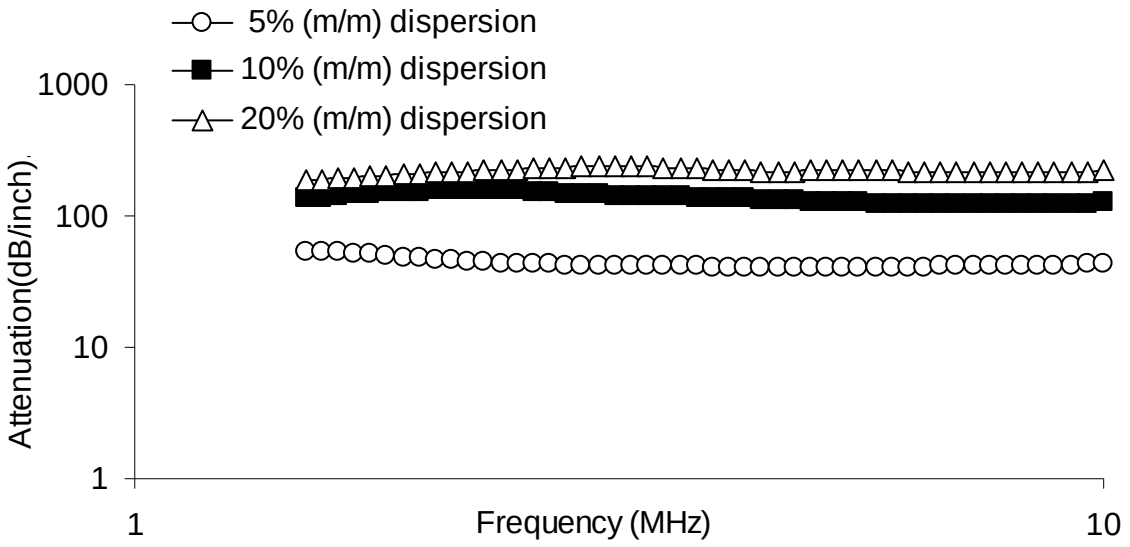


Fig. B. 3(b)

Fig. B. 3: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 5% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 5% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity.



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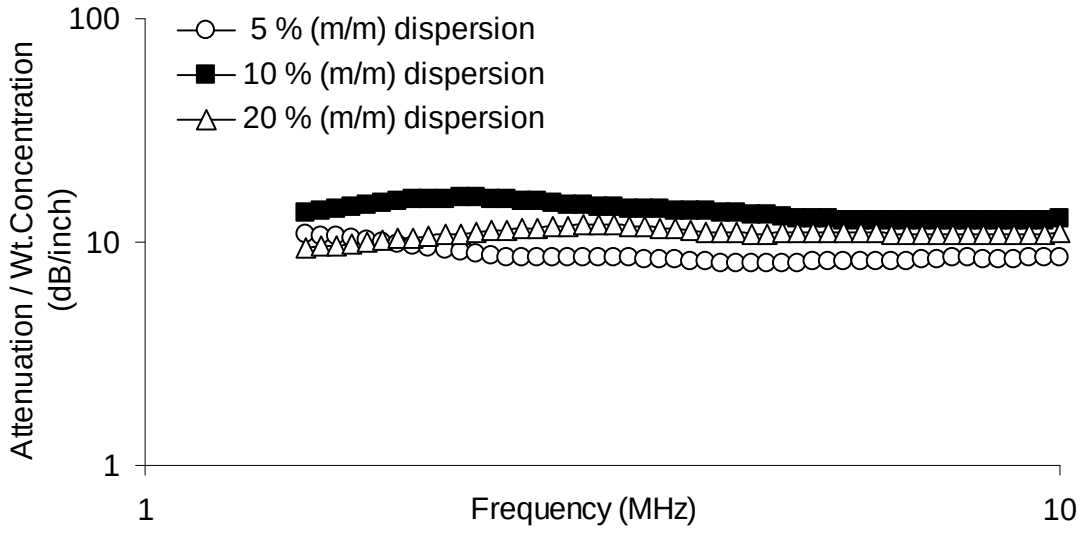

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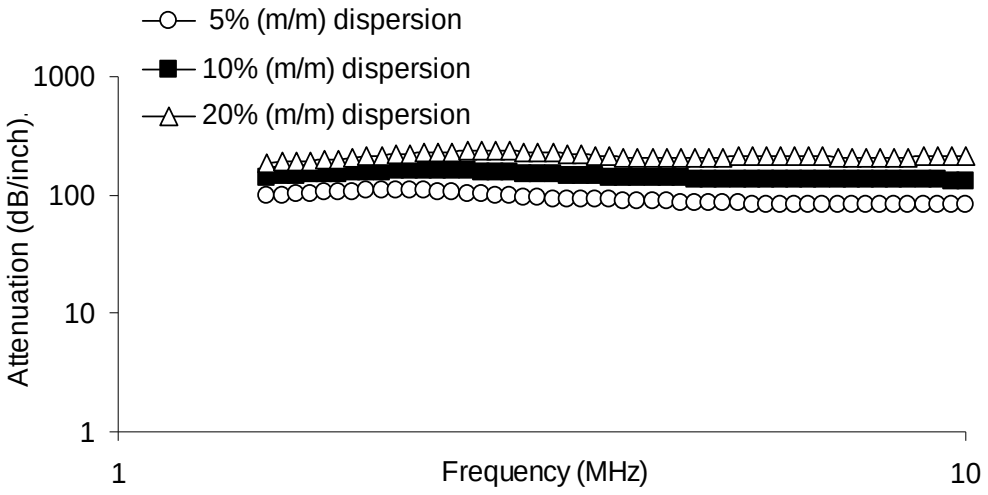
Fig. B. 4: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 10% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 10% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity.



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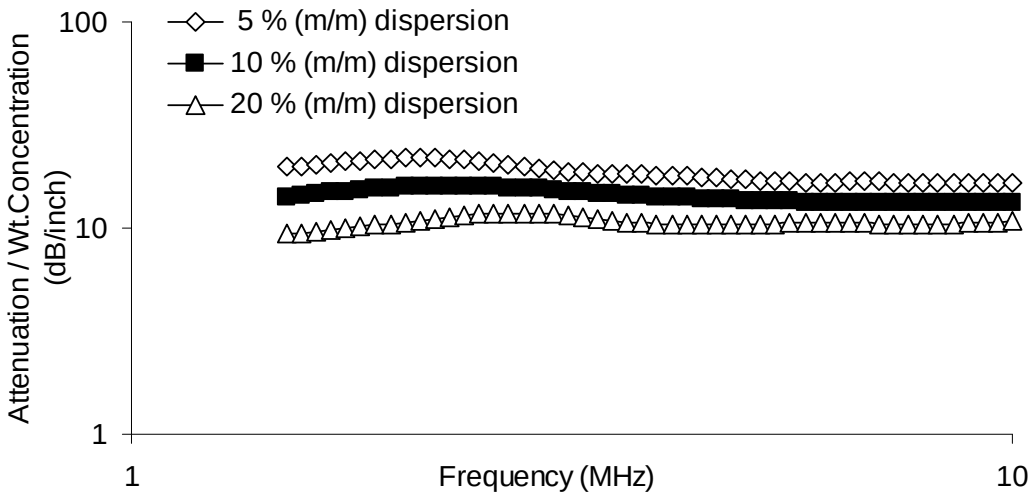


Fig. B. 5(b)

Fig. B. 5: (a) Acoustic attenuation spectra of dispersions of $CaCO_3$ at different concentrations. In each case, 20% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity. (b) The graph shows attenuation per unit concentration vs. frequency for dispersions of $CaCO_3$ at different concentrations. In each case, 20% Sodium polyacrylate of the weight of $CaCO_3$ is present as impurity.

Appendix C

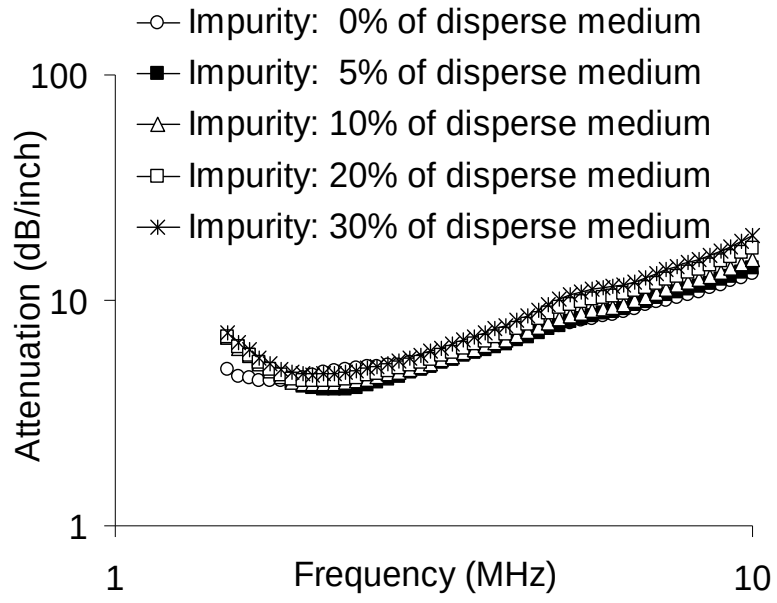
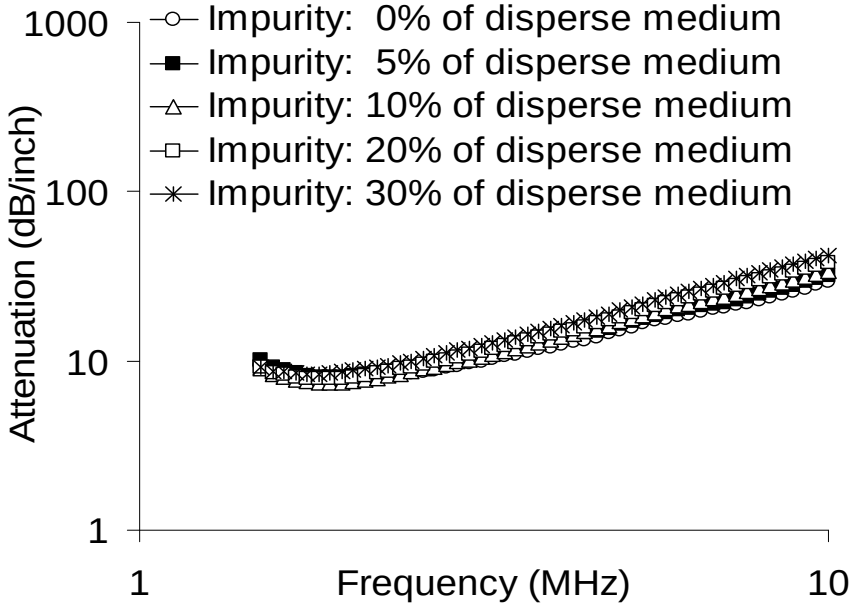


Fig. C. 1(a)



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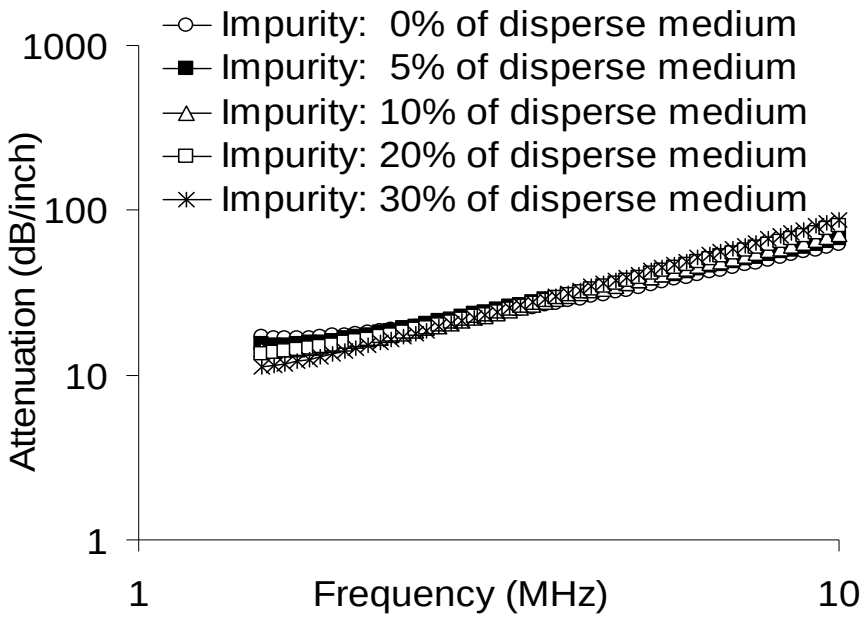

Fig. C. 1(c)

Fig. C. 1: (a) Effects of concentration of impurity of $MgCO_3$ on 5% (m/m) dispersion of $CaCO_3$.(b) Effects of concentration of impurity of $MgCO_3$ on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of $MgCO_3$ on 20% (m/m) dispersion of $CaCO_3$.

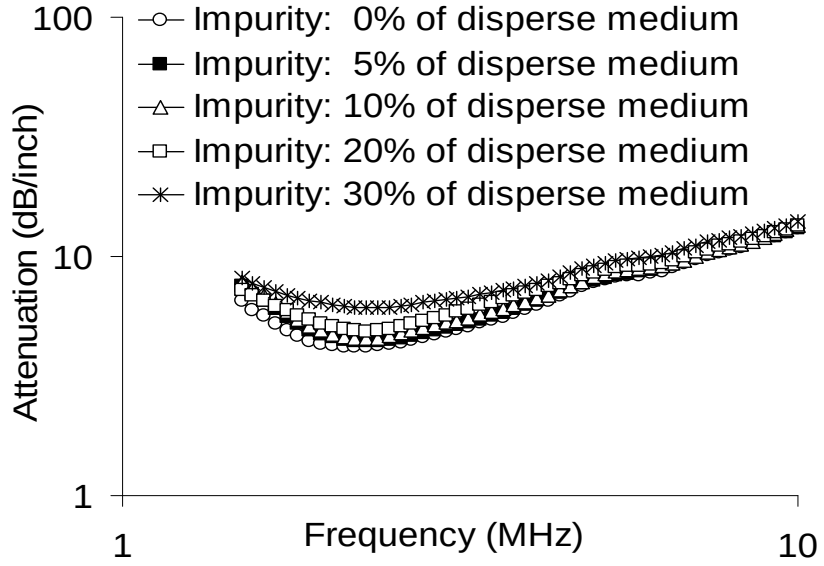

Fig. C. 2(a)

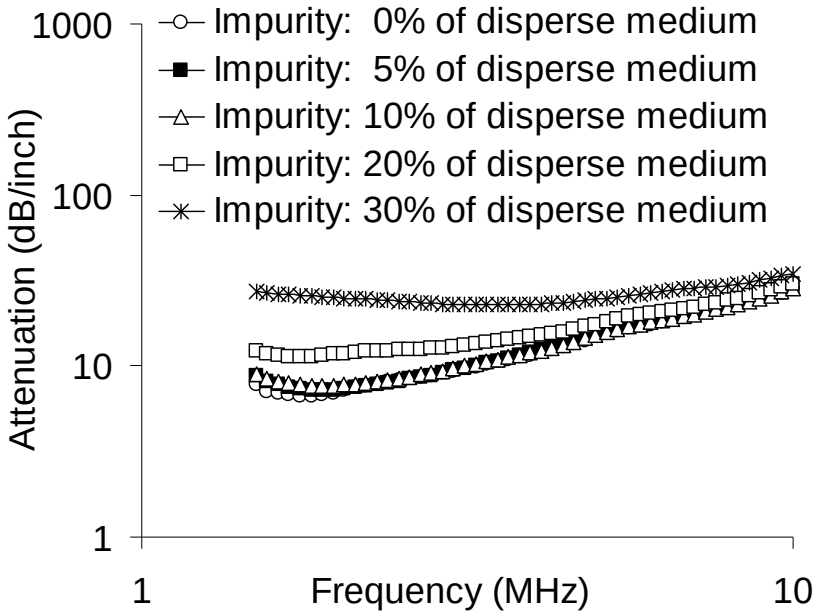

Fig. C. 2(b)

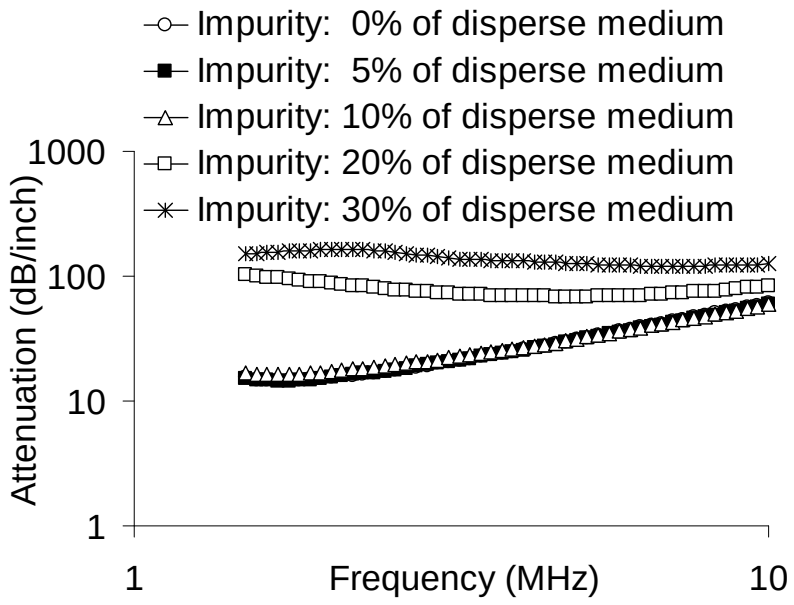

Fig. C. 2(c)

Fig. C. 2: (a) Effects of concentration of impurity of $NaNO_3$ on 5% (m/m) dispersion of $CaCO_3$. (b) Effects of concentration of impurity of $NaNO_3$ on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of $NaNO_3$ on 20% (m/m) dispersion of $CaCO_3$.

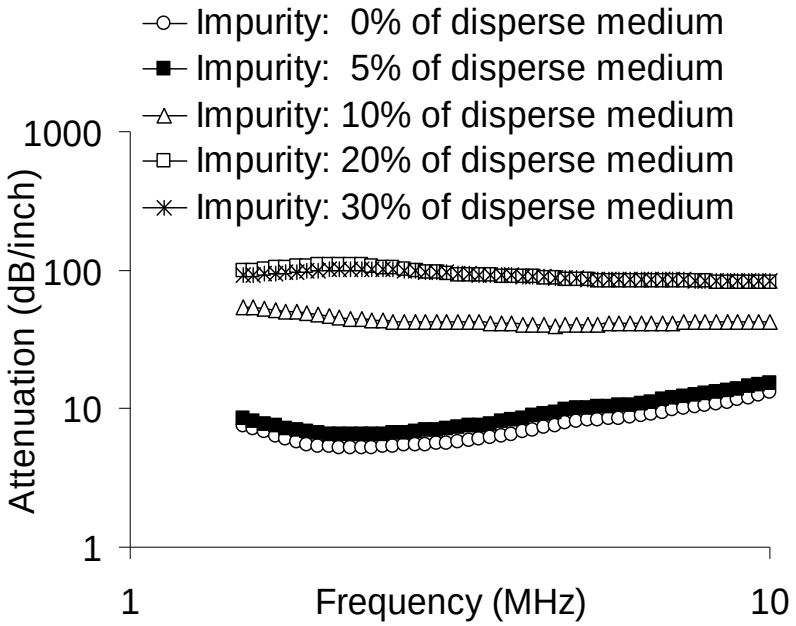

Fig. C. 3(a)

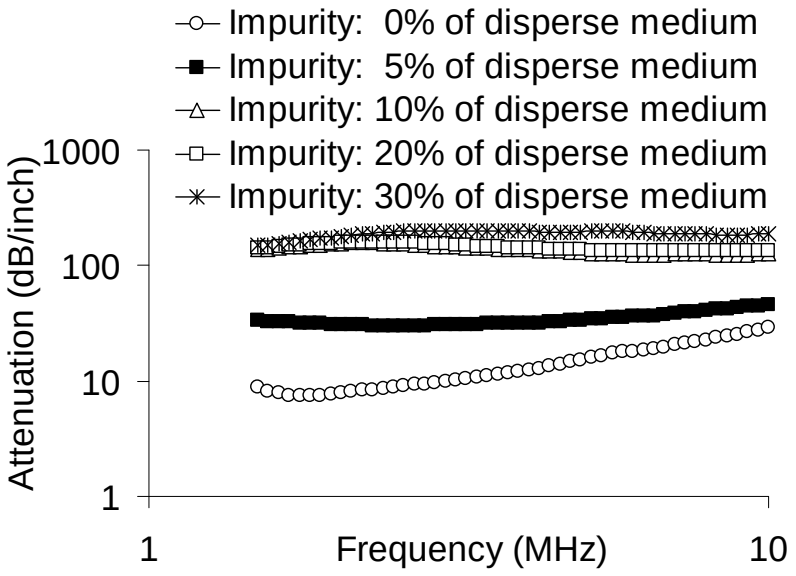

Fig. C. 3(b)

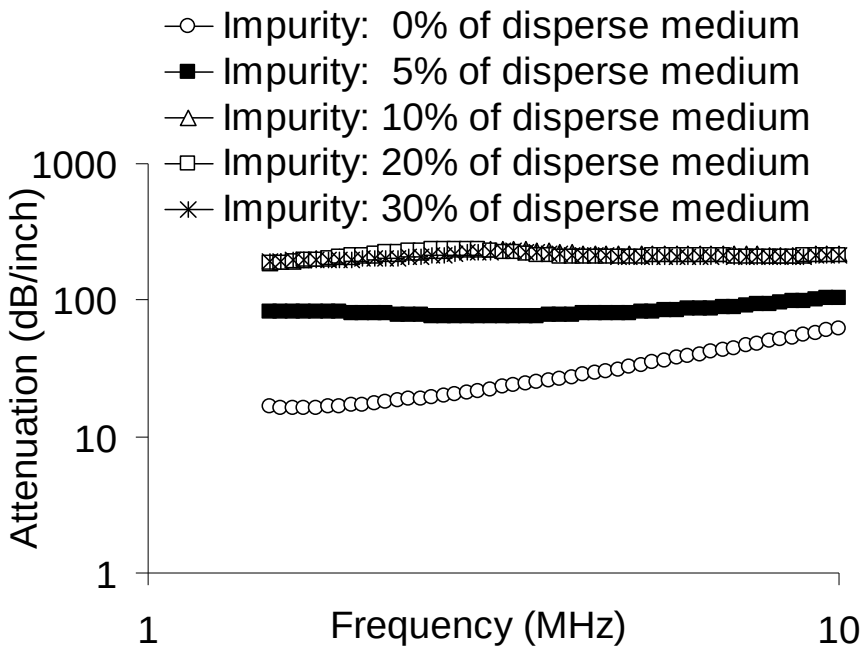

Fig. C. 3(c)

Fig. C. 3: (a) Effects of concentration of impurity of Sodium polyacrylate on 5% (m/m) dispersion of $CaCO_3$. (b) Effects of concentration of impurity of Sodium polyacrylate on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of Sodium polyacrylate on 20% (m/m) dispersion of $CaCO_3$.

Appendix D

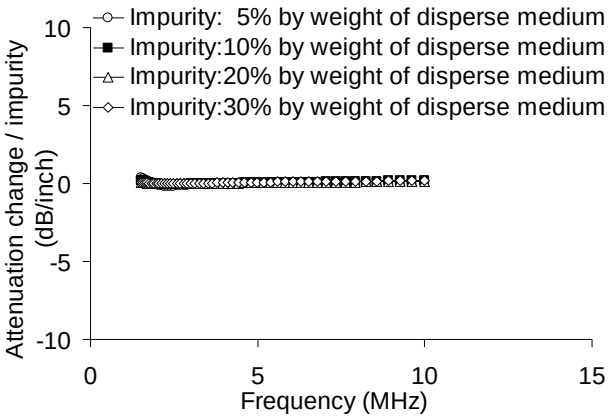

Fig. D. 1(a)

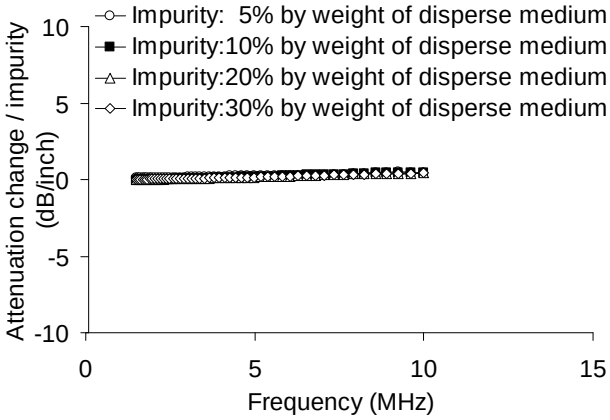

Fig. D. 1(b)

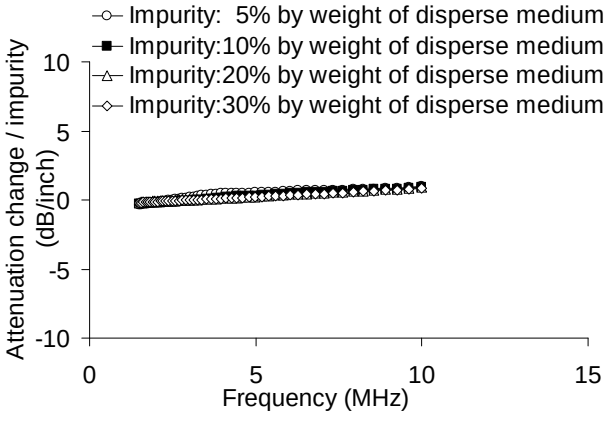

Fig. D. 1(c)

Fig. D. 1: (a) Effects of concentration of impurity of $MgCO_3$ on 5% (m/m) dispersion of $CaCO_3$. (b) Effects of concentration of impurity of $MgCO_3$ on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of $MgCO_3$ on 20% (m/m) dispersion of $CaCO_3$.

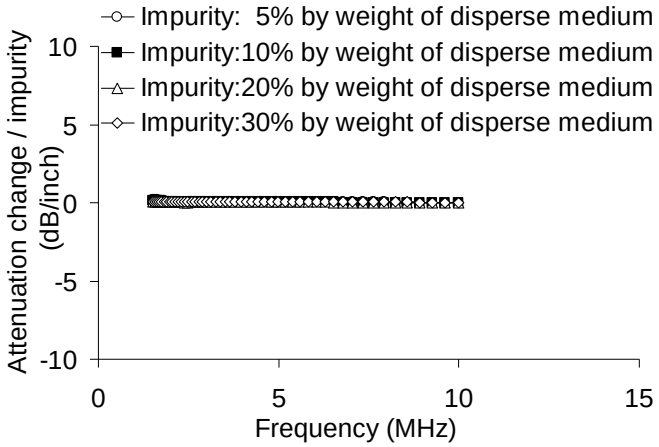

Fig. D. 2(a)

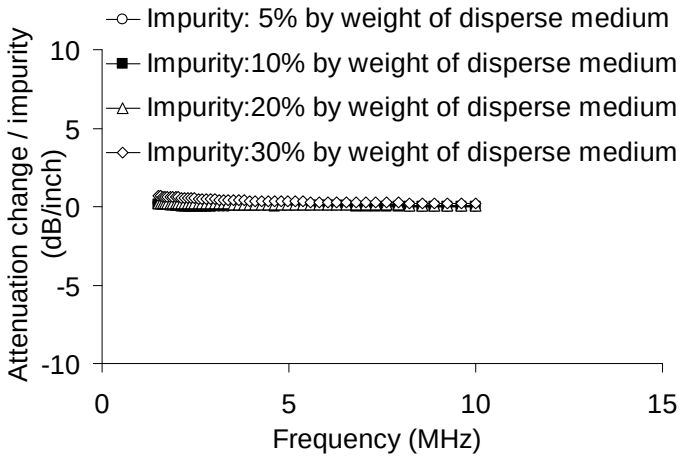

Fig. D. 2(b)

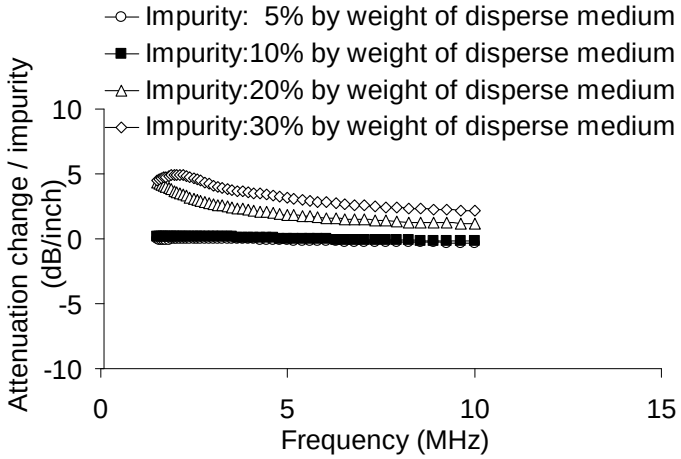

Fig. D. 2(c)

Fig. D. 2: (a) Effects of concentration of impurity of $NaNO_3$ on 5% (m/m) dispersion of $CaCO_3$. (b) Effects of concentration of impurity of $NaNO_3$ on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of $NaNO_3$ on 20% (m/m) dispersion of $CaCO_3$.

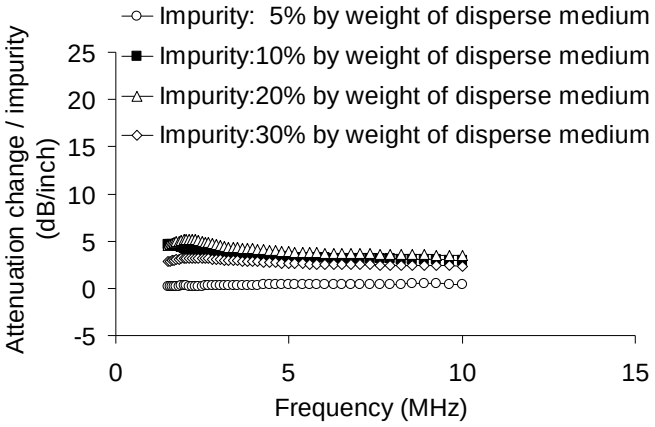

Fig. D. 3(a)

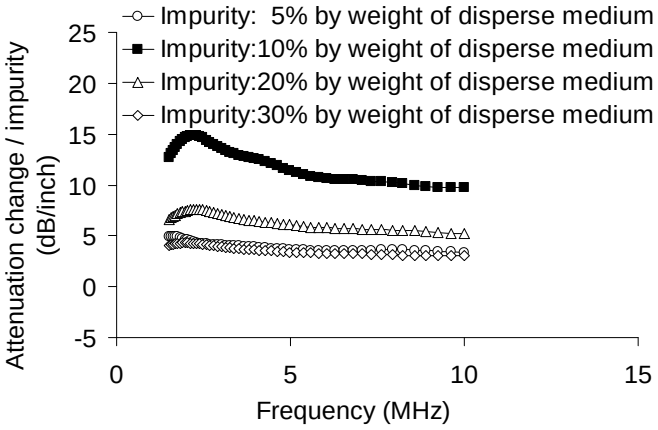

Fig. D. 3(b)

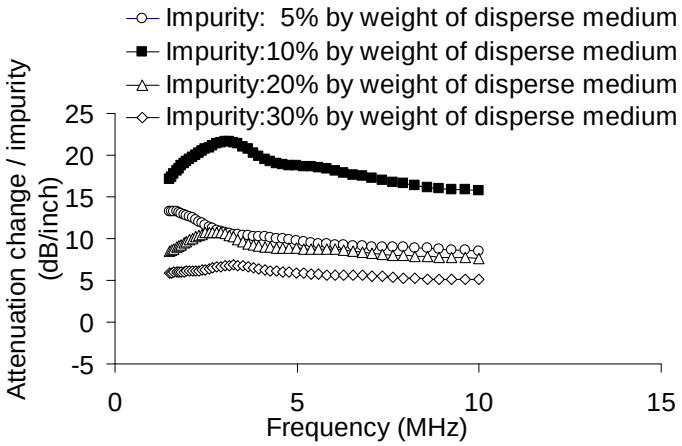

Fig. D. 3(c)

Fig. D. 3: (a) Effects of concentration of impurity of Sodium polyacrylate on 5% (m/m) dispersion of $CaCO_3$. . (b) Effects of concentration of impurity of Sodium polyacrylate on 10% (m/m) dispersion of $CaCO_3$. (c) Effects of concentration of impurity of Sodium polyacrylate on 20% (m/m) dispersion of $CaCO_3$.

Appendix E

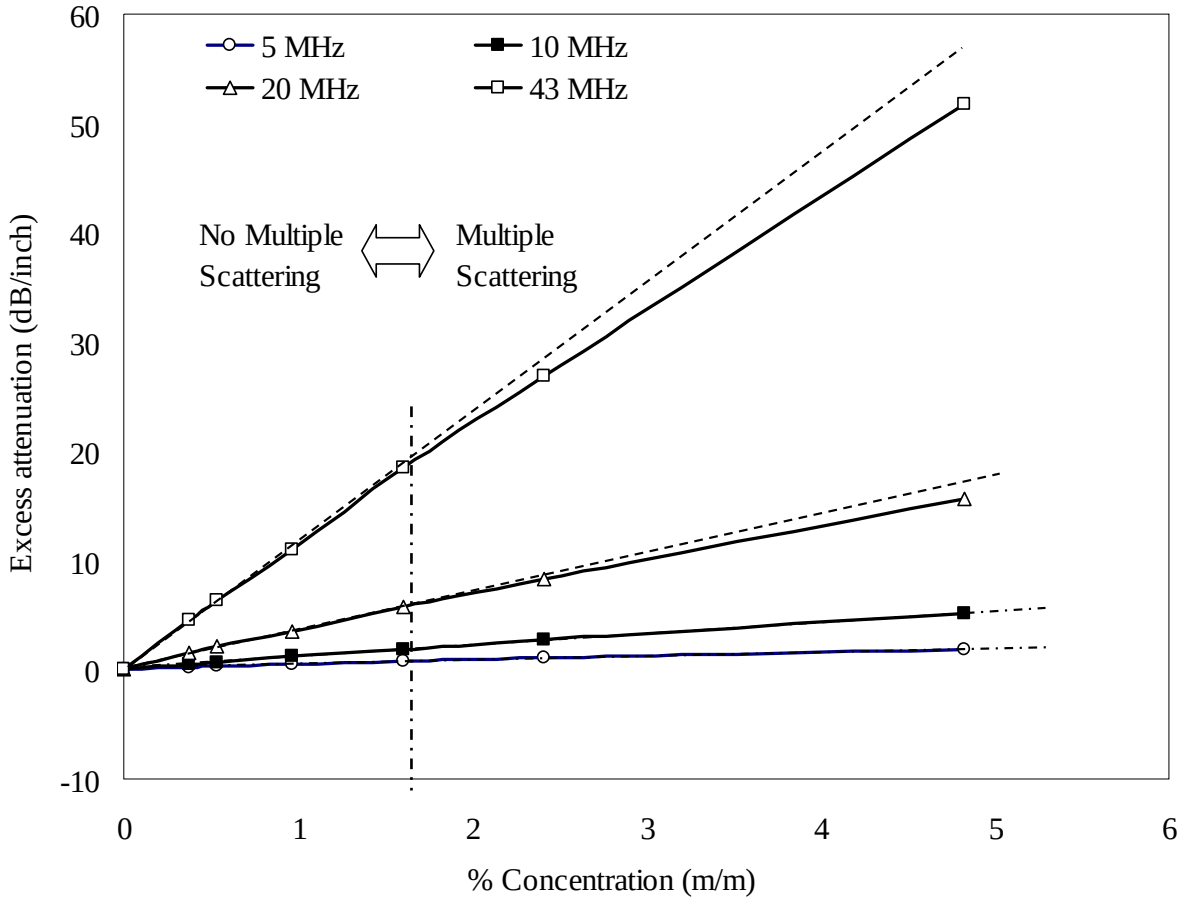

Fig. E. 1: Multiple scattering in 5 % (m/m) dispersion.

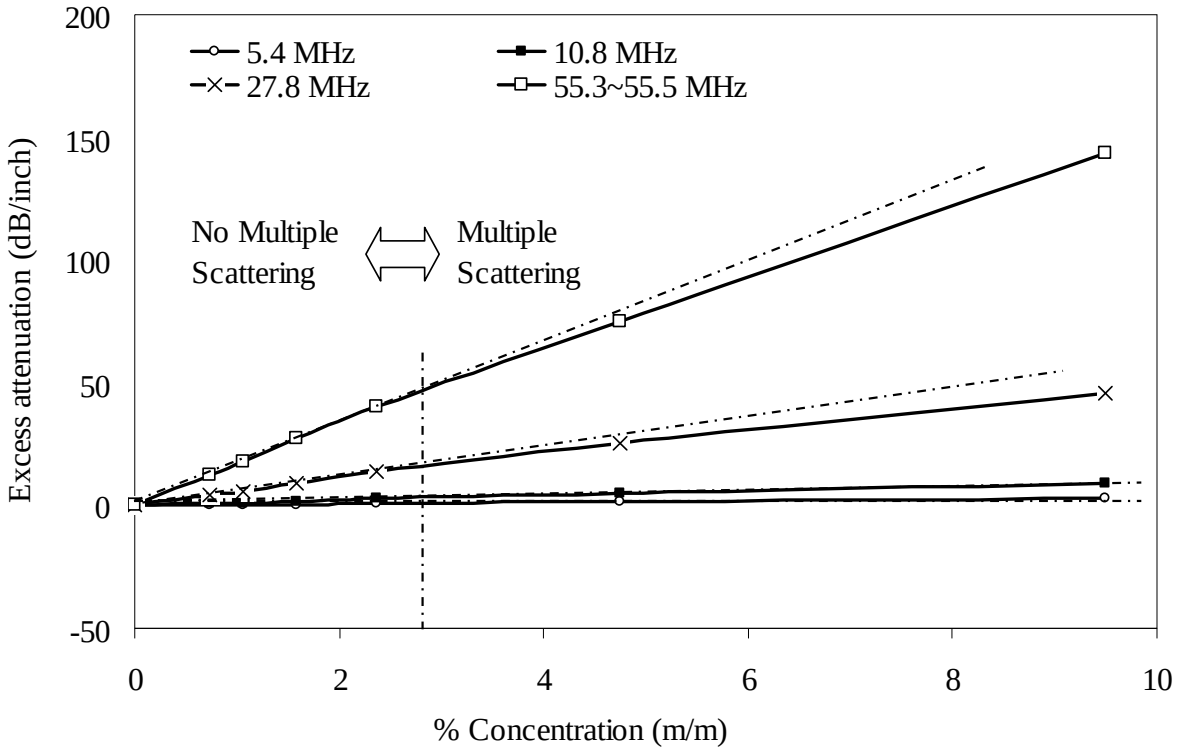

Fig. E. 2: Multiple scattering in 10 % (m/m) dispersion.

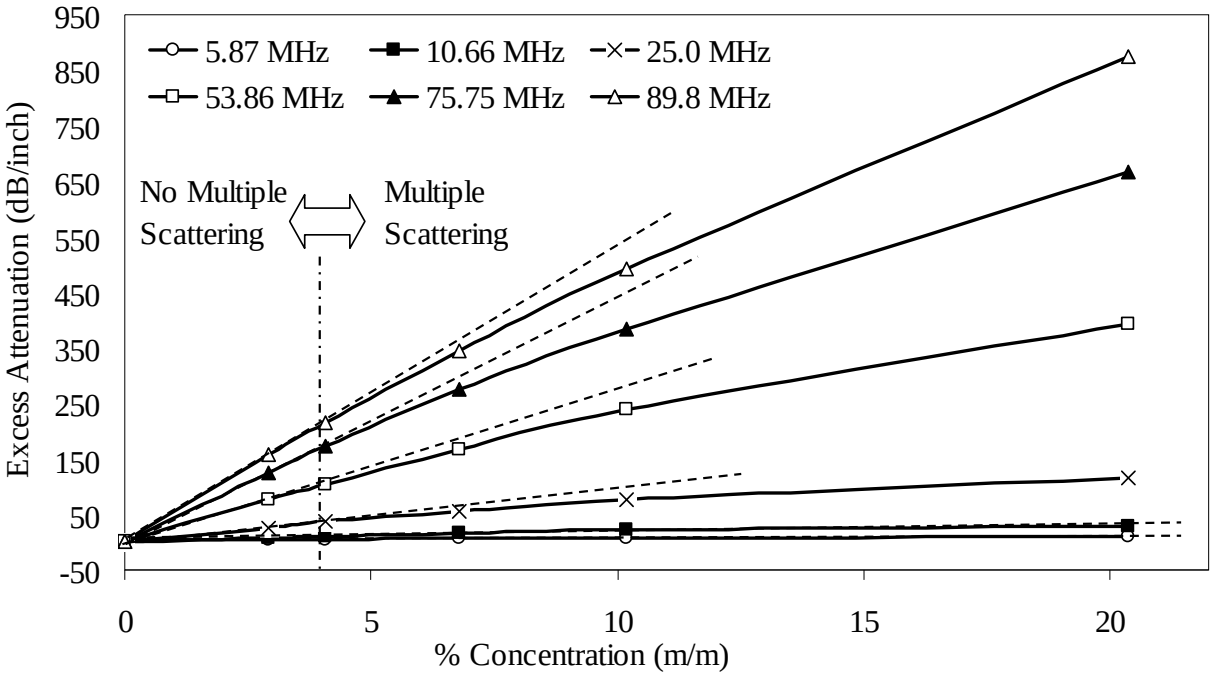

Fig. E. 3: Multiple scattering in 30 % (m/m) dispersion.